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(54) Title: METHOD OF FUEL PRODUCTION FROM FISCHER-TROPSCH PROCESS

(57) Abstract: A process is disclosed for preparing a finished fuel product from a stabilized product mixture, which is produced from the effluent of a Fischer-Tropsch synthesis process. In the process, a Fischer-Tropsch synthesis process is conducted at a site which is remote from the market site where the products from the process are ultimately marketed. The Fischer-Tropsch effluent product is hydroprocessed, and the hydroprocessed effluent separated to remove a C_4- fraction and to yield a stabilized product mixture which can be exported to the market site. At the market site, the stabilized product mixture is fractionated into at least one finished fuel product. A heavy fraction may also be recovered at the market site for separation into at least one lubricating oil base stock and then conversion at hydroisomerization conditions to form a lubricating base oil.

METHOD OF FUEL PRODUCTION FROM FISCHER-TROPSCH PROCESS

Field of the Invention

The present invention is directed to a method for preparing liquid fuel in a hydrocarbon synthesis process, and more specifically for preparing a stabilized mixed fuel from a carbon source at a remote site, and tailoring one or more finished fuel products from the mixed fuel in order to meet local fuel requirements at a market site.

Background of the Invention

Many of the huge natural gas reserves which are targeted for hydrocarbon fuel synthesis processes, such as a Fischer-Tropsch process, methanol synthesis and the like are generally remote from major fuel markets. Consequently, most or all of the products from the synthesis process are exported from the remote site, generally to multiple markets, each with potentially different fuel needs and requirements.

In the conventional synthesis process, a natural gas, coal or heavy oil is generally converted to liquid hydrocarbons at a site adjacent to the natural resource. In the Fischer-Tropsch process, a carbon-based resource is converted to syngas (predominantly CO and H_2) and the syngas converted to a primarily paraffinic hydrocarbon product. In preparing a fuel, the paraffinic hydrocarbons in the conventional process are hydroprocessed to remove at least some of the oxygenates and olefins in the product, to reduce the molecular weight of the product, and to lower the cloud point and/or the pour point of the product. A final distillation step in the conventional process provides the finished fuel and lube product for export to the various markets.

However, the conventional method has several disadvantages. For one, the conventional processes are complex and expensive, with multiple processing steps conducted at the remote site. Developing the site and transporting equipment to the site is generally more costly that using existing processes at a more developed market site. Furthermore, much of the

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product from a remote site process is exported, generally to more than one market site. Each of these market sites have potentially different fuel requirements and needs. Finished fuel product prepared at the remote site must be tailored to meet the specific requirement of each market.

Methods for transporting Fischer-Tropsch derived syncrude from a remote site to a commercial refinery are known in the art (See, for example, U.S. Patent Nos. 5,968,991; 5,945,459; 5,856,261; 5,856,260 and 5,863,856). One approach has been to isolate a C20-36 syncrude and ship this composition as a solid. A limitation of this approach is that it is difficult and expensive to transport solids, because it requires expensive forming, loading and unloading facilities.

Other approaches have focused on transporting syncrude, or a syncrude which has been partially refined to convert some of the linear hydrocarbons into isoparaffins and thus generate a syncrude which is liquid at near ambient temperature. One approach to transporting syncrude in the liquid state involves partially dewaxing the syncrude to form a pumpable liquid (See, for example, U.S. Patent No. 5,292,989). However, this dewaxing may require the construction of facilities which are expensive and difficult to operate in remote locations.

Another approach involves transporting the syncrude as a molten wax. This transportation method does not require the forming, loading and unloading facilities needed to transport solids, or the dewaxing facilities needed to convert the syncrude into a product that is liquid at room temperature. However, Fischer-Tropsch products include a sufficient quantity of volatile hydrocarbons to cause the products to exceed the vapor pressure specifications if the syncrude were shipped at a temperature at which the syncrude is molten.

What is needed is a process for preparing a finished fuel from a remote hydrocarbon synthesis process, while reducing the processing complexity of the process at the remote site. What is also needed is a more effective method for tailoring the final product from the synthesis process for each individual market.

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Brief Description of the Invention

The present invention relates to a Fischer-Tropsch synthesis process, and to an integrated process for preparing a stabilized product mixture, in a Fischer-Tropsch synthesis process, for export to a market location. In the process, a carbonaceous source which is recovered from a remote site is converted through a series of steps into a stabilized product mixture at or near the remote site. At least a portion of stabilized product mixture is then exported to a market location, for a final separation step to produce at least one finished fuel product. More specifically, in the present process, a carbonaceous source, such as natural gas, coal or heavy oil, which is recovered as a resource at a remote site, is converted to a syngas comprising predominantly H_2 and CO. The syngas is further converted to synthetic hydrocarbons in a hydrocarbon synthesis process, and the synthetic hydrocarbon product so produced are converted to a stabilized product mixture for export to a market location. A Fischer-Tropsch synthesis process is the preferred process for preparing the synthetic hydrocarbons.

In the preparation of the stabilized product mixture, the synthetic hydrocarbon product is upgraded via hydroprocessing, at conditions selected to yield a stabilized product mixture which comprises fuel and/or lubricating oil-base stock range products. At least one of the products present in the stabilized product mixture has the properties of a finished fuel product, and can be recovered as such by an additional distillation step.

In one embodiment, the invention provides a method for preparing finished products from a Fischer-Tropsch synthesis process, the method comprising:

(a) reacting a synthesis gas comprising H_2 and CO to form at least one Fischer-Tropsch effluent product;

(b) reacting at least a portion of the Fischer-Tropsch effluent product at hydroprocessing conditions to form a hydroprocessed effluent;

(c) separating at least a portion of the hydroprocessed effluent into at least a C_4- fraction and a stabilized product mixture;

(d) transporting at least a portion of the stabilized product mixture to a market site; and

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(e) separating at least a portion of the stabilized product mixture at the market site into at least one finished fuel product.

In a separate embodiment, the invention provides a method for preparing finished products from a Fischer-Tropsch synthesis process, the method comprising:

a) receiving a stabilized product mixture recovered from a Fischer-Tropsch synthesis process, which stabilized product mixture is prepared by the process comprising:

i) reacting a synthesis gas comprising H_2 and CO to form at least one Fischer-Tropsch effluent product;

ii) reacting at least a portion of the Fischer-Tropsch effluent product at hydroprocessing conditions to form a hydroprocessed effluent;

iii) separating at least a portion of the hydroprocessed effluent into at least a C_4- fraction and a stabilized product mixture; and

iv) transporting at least a portion of the stabilized product mixture to a market site;

b) separating at least a portion of the stabilized product mixture without additional hydroprocessing into at least one finished fuel fraction at the market site;

wherein the stabilized product mixture is prepared at a remote site relative to the market site.

A preferred stabilized product mixture comprises:

(a) greater than 80 wt% paraffins,

(b) less than 200 ppm oxygen as oxygenates,

(c) less than 50 ppm sulfur,

(d) less than 50 ppm nitrogen, and

(e) less than 5% (v/v) olefins.

For mixtures of this type, most or all of the stabilized product mixture is recovered from a step of hydroprocessing.

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Among other factors, the present invention includes Fischer-Tropsch synthesis, upgrading the synthesis product (preferably by one or more of hydrotreating, isomerization and hydrocracking), and stabilizing the resultant full boiling range liquid product. The process further includes separating the full boiling range liquid product to final finished products meeting specification requirements. In the process of the invention, all the major processing steps are conducted at a remote site except for final fractionation, which is conducted at a market site. This invention significantly reduces remote site operating complexity by moving the final distillation step from the remote site to the market site, with equipment suitable for distillation and processing in order to make the finished fuel product. Since final product separation is carried out at the market site, final product separation can be tailored to the particular market to which the stabilized product mixture is exported, rather than being anticipated at the remote site.

Detailed Description of the Invention

This invention is directed to a process for converting remote natural gas to liquid fuels and/or lubricating oil base stocks while minimizing the complexity of the remote site processing, and while minimizing the difficulty and expense of transporting the products from the remote site to a market site. As used herein, the market site represents a site near to the ultimate market for the finished fuel products which are prepared in the process. The market site may be a marketing terminal, or a fractionation terminal or refinery for separating the stabilized product mixture into the finished fuel products. The market site preferably has the capability for producing and/or marketing finished fuels and lubricating oil base stocks.

The Fischer-Tropsch synthesis process is conducted at a remote site, sufficiently separated from the market site so that the stabilized product mixture is transported from the Fischer-Tropsch synthesis process to the market site, using transportation media such as by ship, by truck, by train, by barge, and the like.

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The stabilized product mixture is prepared at a remote site, near the source of the carbonaceous material from which the stabilized product mixture is made, and at a distance from the distillation site at which the material is separated into fuel products for sale. The market site may be a refinery or other existing processing facility with the capability of producing a finished product from the stabilized product mixture. Preferably, the market site comprises a means of distilling the stabilized product mixture into one or more finished fuel products. The remote site is at a location separate from a refinery, distillation site and/or market site and which generally has a higher cost of construction than the cost of construction at the refinery or market. In quantitative terms, the distance between the remote site and the refinery or market (the distance of transportation) is more than 100 miles, preferably more than 500 miles, and most preferably more than 1000 miles. Transportation of the stabilized product mixture is by ship, train, truck transport, pipeline, and the like. Preferably, at least a portion of the transportation of the stabilized product mixture will occur via ship.

The stabilized product mixture is a broad boiling range product, substantially free of C_4- material, and comprising at least one fuel fraction, preferably at least one diesel fraction. In the process, a stabilized product mixture is prepared in a Fischer-Tropsch synthesis process, which includes a Fischer-Tropsch reaction zone and optionally one or more hydroprocessing reaction zones for upgrading the effluent from the Fischer-Tropsch reaction zone and optionally one or more fractionation zones for removing a substantial portion of the C_4- components from the upgraded effluent. This stabilized product mixture is in condition for transportation by, e.g. ship, train, truck transport, pipeline, and the like. In particular, the stabilized product mixture has a true vapor pressures of less than about 15 psia, preferably less than about 11 psia, when measured at its transportation temperature.

The stabilized product mixture, which is recovered from a Fischer-Tropsch synthesis process at a remote site, is then separated into at least one fuel fraction, preferably at least one finished diesel fraction, at a market site which is separate from the remote synthesis process site. The

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stabilized product mixture is preferably prepared at the remote site in such a way that additional hydroprocessing is not necessary at the market site. However, it may be desirable under some conditions to mildly hydrotreat the stabilized product mixture at the market site to remove contaminants accumulated in the product during transportation.

The stabilized product mixture recovered from the Fischer-Tropsch synthesis process is a highly paraffinic mixture, substantially free of C_4-. In the embodiment in which the entire stabilized product mixture is derived from a hydroprocessing step, it will contain few, if any, olefins and heteroatoms. Under these conditions, the preferred product mixture comprises:

i) greater than 80 wt%, preferably greater than 90 wt% and more preferably greater than 95 wt% paraffins;
ii) less than 200 ppm oxygen as oxygenates;
iii) less than 50 ppm sulfur;
iv) less than 50 ppm nitrogen; and
v) less than 5% olefins.

Depending on the boiling range of the stabilized product mixture, the stabilized product mixture may be separated into at least one fuel fraction and further into at least one lubricating oil base stock fraction. The fuel fraction, preferably a fuel fraction boiling in the diesel boiling range, is suitable for use in a diesel engine. The lubricating oil base stock is suitable for hydroisomerization to produce a low pour point, high quality lubricating base oil.

In the Fischer-Tropsch synthesis process, a synthesis gas comprising H_2 and CO are reacted in a Fischer-Tropsch reaction zone over a Fischer-Tropsch catalyst to produce at least one Fischer-Tropsch effluent product. The stabilized product mixture is derived from the effluent of a Fischer-Tropsch reaction zone. In one embodiment of the invention, the stabilized product mixture is recovered directly from a Fischer-Tropsch reaction zone. Either the entire C_5+ effluent, or a fraction thereof, such as one having an endpoint in the range of 650-750°F, are suitable for use in the present invention. When the reaction zone effluent stream contains excess

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C_4- material, thus rendering the effluent unsafe for transportation, some separation of the C_4- material may be required, such as by fractionation, by flash distillation, or by stripping with an inert or hydrocarbonaceous gas.

In a separate embodiment of the invention, a stabilized product mixture is prepared by hydroprocessing at least a portion of at least one Fischer-Tropsch effluent product at hydroprocessing conditions. The effluent stream to be hydroprocessed may be the entire Fischer-Tropsch reaction zone effluent or some fraction thereof (i.e. the total C_5+ effluent from the reaction zone; a light stream boiling in the range of C_5+ to an endpoint in the range of 650-750°F; a wax fraction having an initial boiling point in the range of 650-750°F; or a wax fraction having an initial boiling point in the range of 650-750°F and an end point in the range of 950-1150°F). The hydroprocessing process may include one or more of hydrocracking, hydrotreating and/or hydroisomerization. Fischer-Tropsch reaction zone effluents having an endpoint in the range of 650-750°F may preferably be hydroprocessed using one or both of hydrotreating and hydroisomerization. For such a stream, the oxygenates and olefins which may be present in the effluent stream are saturated by hydrotreating, and the normal paraffins in the effluent stream are at least partially isomerized to low pour products, thus upgrading the stream without overly cracking it to less desirable light products. The 650°-750°F endpoint stream may also be blended without hydroprocessing with a heavier Fischer-Tropsch effluent stream which has been hydroprocessed prior to blending.

A Fischer-Tropsch effluent stream containing components boiling in the range above 650°-750°F may suitably be hydrotreated to remove oxygenates and olefins, and/or hydrocracked to reduce the boiling range of the effluent stream, and/or hydroisomerized to reduce the pour point of the effluent stream and make handling and shipping of the stabilized product mixture derived therefrom easier. A hydroprocessed stabilized product mixture produced in this manner will have the following properties:

i) greater than 80 wt% paraffins (> 90 wt%, > 95 wt%),

ii) less than 200 ppm oxygen as oxygenates,

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iii) less than 50 ppm sulfur,

iv) less than 50 ppm nitrogen, and

v) less than 5% (v/v) olefins.

Following transportation of the stabilized product mixture from the remote site to a more developed site, the stabilized product mixture is fractionated into finished fuel products. Preferably, the stabilized product mixture requires no processing other than fractionation of the stabilized product mixture to make the finished fuel components which are ready for addition of optional additives for sale as finished fuels. The additives which might be added are well known in the art. The additives are proprietary products which vary from vendor to vendor; the choice of any additive is within the scope of the present invention. In some situations it may be desirable to mildly hydroprocess the stabilized product mixture by mild hydrotreating or hydrofinishing, in order to remove oxidation products or contaminants which were introduced to the C_5+ material during transportation. A finished diesel fuel suitable for use in diesel engines conforms to the current version at least one of the following specifications:

- ASTM D 975 – "Standard Specification for Diesel Fuel Oils",
- European Grade CEN 90,
- Japanese Fuel Standards JIS K 2204,
- The United States National Conference on Weights and Measures (NCWM) 1997 guidelines for premium diesel fuel, or
- The United States Engine Manufacturers Association recommended guideline for premium diesel fuel (FQP-1A).

A finished jet fuel suitable for use in turbine engines for aircraft or other uses meets the current version of at least one of the following specifications:

- ASTM D1655-99,
- DEF STAN 91-91/3 (DERD 2494), TURBINE FUEL, AVIATION, KEROSENE TYPE, JET A-1, NATO CODE: F-35,
- International Air Transportation Association (IATA) "Guidance Material for Aviation Turbine Fuels Specifications", 4th edition, March 2000, or

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- United States Military Jet fuel specifications MIL-DTL-5624 (for JP-4 and JP-5) and MIL-DTL-83133 (for JP-8).

Middle distillate fractions as described herein boil in the range of about 250°-700°F (121°-371°C) as determine by the appropriate ASTM test procedure. The term "middle distillate" is intended to include the diesel, jet fuel and kerosene boiling range fractions. The kerosene or jet fuel boiling point range is intended to refer to a temperature range of about 280°-525°F (138°-274°C) and the term "diesel boiling range" is intended to refer to hydrocarbon boiling points of about 250°-700°F (121°-371°C). Gasoline or naphtha is normally the C_5 to 400°F (204°C) endpoint fraction of available hydrocarbons. The boiling point ranges of the various product fractions recovered in any particular refinery or synthesis process will vary with such factors as the characteristics of the source, local markets, product prices, etc. Reference is made to ASTM standards D-975, D-3699-83 and D-3735 for further details on kerosene, diesel and naphtha fuel properties.

A finished lubricating base oil is useful for blending with a specified additive package for preparation of a finished lubricant. A finished lubricating oil base stock is specified by viscosity index, saturate and sulfur specifications. API Publication 1509: Engine Oil Licensing and Certification System, "Appendix E-API Base Oil Interchangeability Guidelines for Passenger Car Motor Oil and Diesel Engine Oils" describes base stock categories. A Group II base stock contains greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and has a viscosity index greater than or equal to 80 and less than 120. A Group III base stock contains greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and has a viscosity index greater than or equal to 120.

The method of the invention will be illustrated by the following exemplary process.

In this example process, a carbonaceous material is converted to a syngas comprising CO and H_2. Typical reforming methods for preparing CO and H_2 from this material include steam reforming, partial oxidation, dry

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reforming, series reforming, convective reforming, and autothermal reforming. Such processes are well known in the art. The syngas is reacted in a Fischer-Tropsch reaction zone to produce a light stream, boiling in the range of C_5+ to an endpoint in the range of 650-750°F, and a wax stream having an initial boiling point in the range of 650-750°F. The wax stream and/or the light stream may be processed in a number of alternative ways to produce the stabilized liquid mixture. Alternatives which may be contemplated include:

1. The wax stream and the light stream may be combined to make a blend feed stream, and the blend feed stream contacted in a hydrocracking reaction zone. The blend feed stream may optionally be hydrotreated prior to hydrocracking. At least a portion of the hydrocracker reaction zone effluent is passed to a fractionator, wherefrom a C_4- fraction and a C5+ fraction are recovered. The C_5+ fraction is a stabilized product mixture which is suitable for transporting from the remote site to a market site for fractionation to prepare finished fuel products.
2. At least a portion of the hydrocracking reaction zone effluent is passed to a fractionator, and a C_4- fraction, a C_5+ fraction boiling in the range of C_5+ to an endpoint in the range of 650-750°F, and a heavy effluent having an initial boiling point in the range of 650-750°F is recovered therefrom. In this embodiment, the heavy effluent may be recycled to the hydrocracking reaction zone for additional conversion, or transported separately to the market site for production of lubricating oil base stocks.
3. At least a portion of the wax stream is contacted with a hydrocracking catalyst in a hydrocracking reaction zone, and at least a portion the light stream is contacted with a hydrotreating catalyst in a hydrotreating reaction zone. At least a portion of the hydrocracking reaction zone effluent is blended with a portion of the hydrotreating reaction zone effluent, and the blend is passed to a fractionation zone and a C_4- fraction and a C_5+ fraction are recovered therefrom. The C_5+ fraction is a stabilized product mixture which is suitable for transporting from the remote site to a market site for further upgrading and/or fractionation to

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prepare finished fuel products and, optionally, one or more lubricating oil base stocks.

4. At least a portion of the wax stream is contacted with a hydrocracking catalyst in a hydrocracking reaction zone. At least a portion of the hydrocracking reaction zone effluent is blended with a portion of the light stream, and the blend is passed to a fractionation zone and a C_4- fraction and a C_5+ fraction are recovered therefrom. The C_5+ fraction is a stabilized product mixture which is suitable for transporting from the remote site to a market site for further upgrading and/or fractionation to prepare finished fuel products and, optionally, one or more lubricating oil base stocks.
5. At least a portion of the wax stream is contacted in a hydrocracking reaction zone, and at least a portion of the light stream is combined with the effluent from the hydrocracking reaction zone and the blend stream contacted in a hydrotreating reaction zone. At least a portion of the hydrotreating reaction zone effluent is passed to a fractionator and a C_4- fraction and a C_5+ fraction are recovered therefrom. The C_5+ fraction is a stabilized product mixture which is suitable for transporting from the remote site to a market site for further upgrading and/or fractionation to prepare finished fuel products and, optionally, one or more lubricating oil base stocks.

Additional alternatives for hydroprocessing the various streams produced in a Fischer-Tropsch process, including combinations of the alternatives recited above, are considered to be within the scope of the present invention.

The various process steps which may be useful in the present invention are now described in greater detail.

A Fischer-Tropsch process is the preferred method for converting the carbon-based resource to the stabilized product mixture. Catalysts and conditions for performing Fischer-Tropsch synthesis are well known to those of skill in the art, and are described, for example, in EP 0 921 184 A1, the contents of which are hereby incorporated by reference in their entirety. In the Fischer-Tropsch synthesis process, liquid and gaseous hydrocarbons are

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formed by contacting a synthesis gas (syngas) comprising a mixture of H_2 and CO with a Fischer-Tropsch catalyst under suitable reaction temperature and reaction pressure conditions. The Fischer-Tropsch reaction is typically conducted at temperatures of from about 300° to 700°F (149° to 371°C) preferably from about 400° to 550°F (204° to 228°C); pressures of from about 10 to 600 psia, (0.7 to 41 bars) preferably 30 to 300 psia, (2 to 21 bars) and catalyst space velocities of from about 100 to 10,000 cc/g/hr., preferably 300 to 3,000 cc/g/hr.

The products may range from C_1 to C_{200}+ with a majority in the C_5 to C_{100}+ range. The reaction can be conducted in a variety of reactor types, for example, fixed bed reactors containing one or more catalyst beds; slurry reactors; fluidized bed reactors; and a combination of different type reactors. Such reaction processes and reactors are well known and documented in the literature. A slurry Fischer-Tropsch process, which is a preferred process in the practice of the invention, utilizes superior heat (and mass) transfer characteristics for the strongly exothermic synthesis reaction and is able to produce relatively high molecular weight, paraffinic hydrocarbons when using a cobalt catalyst.

In a slurry process, a syngas comprising a mixture of H_2 and CO is bubbled up as a third phase through a slurry in a Fischer-Tropsch reactor. The reactor contains particulate Fischer-Tropsch type hydrocarbon synthesis catalyst dispersed and suspended in a slurry liquid comprising hydrocarbon products of the synthesis reaction which are liquid at the reaction conditions. The mole ratio of the hydrogen to the carbon monoxide may broadly range from about 0.5 to 4, but is more typically within the range of from about 0.7 to 2.75 and preferably from about 0.7 to 2.5. A particularly preferred Fischer-Tropsch process is taught in EP 0609079, herein incorporated by reference in its entirety.

Suitable Fischer-Tropsch catalysts comprise one or more Group VIII catalytic metals such as Fe, Ni, Co, Ru and Re. Additionally, a suitable catalyst may contain a promoter. Thus, a preferred Fischer-Tropsch catalyst comprises effective amounts of cobalt and one or more of Re, Ru, Pt, Fe, Ni,

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Th, Zr, Hf, U, Mg and La on a suitable inorganic support material, preferably one which comprises one or more refractory metal oxides. In general, the amount of cobalt present in the catalyst is between about 1 and about 50 weight percent of the total catalyst composition. The catalysts can also contain basic oxide promoters such as ThO_2, La_2O_3, MgO, and TiO_2, promoters such as ZrO_2, noble metals (Pt, Pd, Ru, Rh, Os, Ir), coinage metals (Cu, Ag, Au), and other transition metals such as Fe, Mn, Ni, and Re. Support materials including alumina, silica, magnesia and titania or mixtures thereof may be used. Preferred supports for cobalt containing catalysts comprise titania. Useful catalysts and their preparation are known

At least one of the products recovered as a Fischer-Tropsch reaction zone effluent is useful in preparing the stabilized product mixture.

In a specific embodiment of the invention, the products from Fischer-Tropsch reactions performed in slurry bed reactors include a light product and a waxy product. The light product (i.e. the condensate fraction) includes hydrocarbons boiling below about 700°F (e.g., tail gases through middle distillates), largely in the C_5-C_{20} range, with decreasing amounts up to about C_{30}. The waxy product (i.e. the wax fraction) includes hydrocarbons boiling above about 650°F (e.g., vacuum gas oil through heavy paraffins), largely in the C_{20}+ range, with decreasing amounts down to C_{10}. Both the light product and the waxy product are substantially paraffinic. The waxy product generally comprises greater than 70% normal paraffins, and often greater than 80% normal paraffins, sometimes approaching 100% normal paraffins. The light product comprises paraffinic products with a significant proportion of alcohols and olefins. In some cases, the light product may comprise as much as 50%, and even higher, alcohols and olefins.

There are a number of hydroprocessing processes which may be used in preparing the Fischer-Tropsch reaction zone effluent as the stabilized product mixture.

During hydrocracking, a hydrocracking reaction zone is maintained at conditions sufficient to effect a boiling range conversion of the VGO feed to the hydrocracking reaction zone, so that the liquid hydrocrackate recovered

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from the hydrocracking reaction zone has a normal boiling point range below the boiling point range of the feed. Typical hydrocracking conditions include: reaction temperature, 400°F-950°F (204°C-510°C), preferably 650°F-850°F (343°C-454°C); reaction pressure 500 to 5000 psig (3.5-34.5 MPa), preferably 1500-3500 psig (10.4-24.2 MPa); LHSV, 0.1 to 15 hr^{-1} (v/v), preferably 0.25-2.5 hr^{-1}; and hydrogen consumption 500 to 2500 scf per barrel of liquid hydrocarbon feed (89.1-445 m^3 H_2 /m^3 feed). The hydrocracking catalyst generally comprises a cracking component, a hydrogenation component and a binder. Such catalysts are well known in the art. The cracking component may include an amorphous silica/alumina phase and/or a zeolite, such as a Y-type or USY zeolite. The binder is generally silica, alumina, or a combination thereof. The hydrogenation component will be a Group VI, Group VII, or Group VIII metal or oxides or sulfides thereof, preferably one or more of molybdenum, tungsten, cobalt, or nickel, or the sulfides or oxides thereof. If present in the catalyst, these hydrogenation components generally make up from about 5% to about 40% by weight of the catalyst. Alternatively, platinum group metals, especially platinum and/or palladium, may be present as the hydrogenation component, either alone or in combination with the base metal hydrogenation components molybdenum, tungsten, cobalt, or nickel. If present, the platinum group metals will generally make up from about 0.1% to about 2% by weight of the catalyst.

In general, hydrotreating reaction conditions are milder than those of hydrocracking, and are intended primarily for olefin and aromatic (if present in the reactant stock) saturation and for heteroatom (oxygen and, if present, sulfur and nitrogen) removal. Catalysts suitable for hydrotreating are designed with a relatively stronger hydrogenation function and a relatively weaker cracking function. Mild hydrotreating, for example to remove color bodies and sources of instability from lubricating base oils, is conducted at the lower hydrotreating temperatures. Hydrotreating conditions include a reaction temperature between 400°F-900°F (204°C-482°C), preferably 650°F-850°F (343°C-454°C); a pressure between 500 to 5000 psig (pounds per square inch gauge) (3.5-34.6 MPa), preferably 1000 to 3000 psig (7.0-20.8 MPa); a

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feed rate (LHSV) of 0.5 hr^{-1} to 20 hr^{-1} (v/v); and overall hydrogen consumption 300 to 2000 scf per barrel of liquid hydrocarbon feed (53.4-356 m^3 H_2 /m^3 feed). The hydrotreating catalyst for the beds will typically be a composite of a Group VI metal or compound thereof, and a Group VIII metal or compound thereof supported on a porous refractory base such as alumina. Examples of hydrotreating catalysts are alumina-supported cobalt-molybdenum, nickel sulfide, nickel-tungsten, cobalt-tungsten and nickel-molybdenum. Typically such hydrotreating catalysts are presulfided.

When treating a substantially paraffinic feedstock, hydroisomerization reactions isomerize the paraffin molecules to improve low temperature properties, e.g. pour and cloud point, of the product. While substantial hydrocracking may occur during hydroisomerization, the two processes are differentiated in the present process by the reduced molecular weight conversion which occurs during hydroisomerization. Typical hydroisomerization conditions are well known in the literature and can vary widely. Isomerization processes are typically carried out at a temperature between 200°F and 700°F, preferably 300°F to 650°F, with a LHSV between 0.1 and 10 hr^{-1}, preferably between 0.25 and 5 hr^{-1}. Hydrogen is employed such that the mole ratio of hydrogen to hydrocarbon is between 1:1 and 15:1. Catalysts useful for isomerization processes are generally bifunctional catalysts that include a dehydrogenation/ hydrogenation component and an acidic component. The acidic component may include one or more of amorphous oxides such as alumina, silica or silica-alumina; a zeolitic material such as zeolite Y, ultrastable Y, SSZ-32, Beta zeolite, mordenite, ZSM-5 and the like, or a non-zeolitic molecular sieve such as SAPO-11, SAPO-31 and SAPO-41. The acidic component may further include a halogen component, such as fluorine. The hydrogenation component may be selected from the Group VIII noble metals such as platinum and/or palladium, from the Group VIII non-noble metals such as nickel and tungsten, and from the Group VI metals such as cobalt and molybdenum. If present, the platinum group metals will generally make up from about 0.1% to about 2% by weight of the catalyst.

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If present in the catalyst, the non-noble metal hydrogenation components generally make up from about 5% to about 40% by weight of the catalyst.

A lubricating base oil is prepared from a heavy fraction having an initial boiling point in the range of 650-750°F. The heavy fraction may be transported as a component of the stabilized product mixture or it may be transported separately from the remote site. If in combination, the heavy fraction is recovered from the stabilized product mixture as a distillate or bottoms fraction during fractionation of the stabilized product mixture at the market site. In general, the heavy fraction will be hydroprocessed at the market site in the preparation of lubricating base oil. An example process includes fractionating the heavy fraction into one or more lubricating oil base stocks, hydroisomerizing each base stock individually, optionally dewaxing to remove residual amounts of wax, and mild hydrotreating to remove unstable compounds and color bodies in the preparation of the high quality, low pour point lubricating base oils. The lubricating oil base stock, which is the feedstock to the hydroisomerization step, may be the whole heavy fraction and a fraction thereof. Suitable fractions include a broad boiling fraction having an initial boiling point in the range of 650-750°F and an end point in the range of 950-1050°F. Narrow boiling fractions are also suitable feedstocks to the hydroisomerization step. These narrow fractions are generally represented by viscosity (e.g. 4 cSt, 6 cSt, 12 cSt and the like) and have a boiling range extent of between 75°F and 200°F. An example narrow fraction has an initial boiling point in the range of 650-750°F and an end point in the range of 750-850°F.

Those skilled in the art will recognize or be able to ascertain using no more than routine experimentation many equivalents to the specific embodiments of the invention described herein. Such equivalents are intended to be encompassed by the following claims.

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WHAT IS CLAIMED IS:

1. A method for preparing finished products from a Fischer-Tropsch synthesis process, the method comprising:
   a) reacting a synthesis gas comprising H_2 and CO to form at least one Fischer-Tropsch effluent product;
   b) reacting at least a portion of the Fischer-Tropsch effluent product at hydroprocessing conditions to form a hydroprocessed effluent;
   c) separating at least a portion of the hydroprocessed effluent into at least a C_4- fraction and a stabilized product mixture;
   d) transporting at least a portion of the stabilized product mixture to a market site; and
   e) separating at least a portion of the stabilized product mixture at the market site into at least one finished fuel product.
2. The method according to Claim 1 wherein the Fischer-Tropsch effluent product is a C_5+ product.
3. The method according to Claim 1 wherein the hydroprocessing conditions includes hydrocracking conditions.
4. The method according to Claim 1 wherein the at least one finished fuel product is a diesel fuel.
5. The method according to Claim 1 wherein the stabilized product mixture is separated at the market site into at least one finished fuel product and a heavy fraction.
6. The method according to Claim 5 wherein the heavy fraction has an initial boiling point in the range of 650-750°F.
7. The method according to Claim 5 wherein the heavy fraction is separated into at least one lubricating oil base stock; and wherein the lubricating oil base stock is converted at hydroisomerization conditions to form a lubricating base oil.
8. The method according to Claim 6 wherein the heavy fraction has a boiling endpoint in the range of 950°F-1100°F.

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9. The method according to Claim 1 wherein the stabilized product mixture boils in the range of C_5 to an endpoint in the range of 650-750°F.

10. The method according to Claim 1 wherein the hydroprocessed effluent is separated into at least a C_4- fraction, a stabilized product mixture and a heavy effluent.

11. The method according to Claim 10 wherein at least a portion of the heavy effluent is combined with at least a portion of the Fischer-Tropsch effluent product for reaction at hydroprocessing conditions.

12. The method according to Claim 10 wherein the hydroprocessing conditions includes hydrocracking conditions.

13. The method according to Claim 10 wherein the stabilized product mixture boils in the range of C_5 to an endpoint in the range of 650-750°F.

14. The method according to Claim 13 wherein the at least one finished fuel product is a diesel fuel.

15. A method for preparing finished products from a Fischer-Tropsch synthesis process, comprising:

a) receiving a stabilized product mixture recovered from a Fischer-Tropsch synthesis process, which stabilized product mixture is prepared by the process comprising:

i) reacting a synthesis gas comprising H_2 and CO to form at least one Fischer-Tropsch effluent product;

ii) reacting at least a portion of the Fischer-Tropsch effluent product at hydroprocessing conditions to form a hydroprocessed effluent;

iii) separating at least a portion of the hydroprocessed effluent into at least a C_4- fraction and a stabilized product mixture; and

iv) transporting at least a portion of the stabilized product mixture to a market site;

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b) separating at least a portion of the stabilized product mixture without additional hydroprocessing into at least one finished fuel fraction at the market site;

wherein the stabilized product mixture is prepared at a remote site relative to the market site.

16. The method according to Claim 15 wherein the stabilized product mixture comprises:

a) greater than 80 wt% paraffins,

b) less than 200 ppm oxygen as oxygenates,

c) less than 50 ppm sulfur,

d) less than 50 ppm nitrogen, and

e) less than 5% (v/v) olefins;

17. The method according to Claim 15 wherein the finished fuel product is a diesel fuel.

18. The method according to Claim 15 wherein the stabilized product mixture is a C_5+ product.

19. The method according to Claim 15 wherein the stabilized product mixture is further separated into a heavy fraction having an initial boiling point in the range of 650-750°F.

20. The method according to Claim 19 wherein the heavy fraction is separated into at least one lubricating oil base stock; and wherein the lubricating oil base stock is converted at hydroisomerization conditions to form a lubricating base oil.

21. The method according to Claim 15 wherein the stabilized product mixture comprises greater than 90 wt% paraffins.

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WO 02/094426 A3

(54) Title: METHOD OF FUEL PRODUCTION FROM FISCHER-TROPSCH PROCESS

(57) Abstract: A process is disclosed for preparing a finished fuel product from a stabilized product mixture, which is produced from the effluent of a Fischer-Tropsch synthesis process. In the process, a Fischer-Tropsch synthesis process is conducted at a site which is remote from the market site where the products from the process are ultimately marketed. The Fischer-Tropsch effluent product is hydroprocessed, and the hydroprocessed effluent separated to remove a C_4- fraction and to yield a stabilized product mixture which can be exported to the market site. At the market site, the stabilized product mixture is fractionated into at least one finished fuel product. A heavy fraction may also be recovered at the market site for separation into at least one lubricating oil base stock and then conversion at hydroisomerization conditions to form a lubricating base oil.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/15748

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7) : C07C 27/00; C10G 73/00, 35/00, 47/00; C07C 7/20,
US CL : 518/700; 208/24, 133, 107; 585/1, 899
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EAST, WEST AND CAS ONLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 97/12118 A1 (DEN NORSKE STATS OLJESELSKAP A.S.) 03 April 1997(03.04.97), page 12, lines 32-39, page 13, lines 1-38 and page 25, lines 25-36.	1-21
Y,P	US 6,294,076 B1 (GENETTI ET AL) 25 September 2001(25.09.01), entire document.	1-21
Y	US 5,766,274 A (WITTENBRINK ET AL) 16 June 1998(16.06.98), entire document.	1-21

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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selective system by the Claus sulfur-recovery process [76].

The Rectisol process is licensed by Lurgi and employed in the SASOL complexes in South Africa [77], [78]; methanol is the adsorbent at low temperature. The Selexol process, licensed by Allied Chemical, uses poly(ethylene glycol) dimethyl ether [77], [78]. The Lurgi Purisol process uses *N*-methyl-2-pyrrolidine (NMP) [77], [78], and the Fluor solvent process uses propylene carbonate [78].

Chemical absorption systems primarily use amines or carbonates to neutralize acidic gases:

$$2\,RNH_2 + H_2O + CO_2 \longrightarrow (RNH_3)_2 \cdot CO_3$$

$$RNH_2 + H_2S \longrightarrow RNH_3 \cdot HS$$

$$RNH_2 + HCN \longrightarrow RNH_3 \cdot CN$$

Heat reverses these reactions, liberating the gases [67].

Carbonates are neutralized as follows:

$$K_2CO_3 + H_2S \longrightarrow KHCO_3 + KHS$$

Carbonyl sulfide (COS) is hydrolyzed to CO_2 and H_2S [77]; the latter is absorbed by the carbonate solution.

The principal chemical absorption processes are Benfield and Catacarb, both potassium carbonate systems [67], and diisopropanolamine (ADIP) [67], *N*-methyldiethanolamine (MDEA) [67], Sulfiban [67], Fluor Econamine [78], and monoethanolamine (MEA) [78], all amine systems.

After purification and shift of the hydrogen: carbon monoxide ratio, the synthesis gas can be converted to hydrocarbons.

2.2. Fischer – Tropsch Synthesis

The Fischer – Tropsch synthesis is a nonselective process that produces a wide range of compounds containing from 1 to > 100 carbon atoms. Only C_1 compounds can be produced with 100 % selectivity. Selectivity can also be high for high molecular mass wax. However, for intermediate products, only certain maximum values are possible; in general selectivities are interrelated [57], [79]. All postulated mechanisms assume that the synthesis occurs by a stepwise growth of hydrocarbon chains, one carbon being added at a time. A probability mechanism of this chain growth, which limits production of gasoline and diesel fuel hydrocarbons (see Section 2.2.3), can be calculated.

At SASOL I in South Africa, iron-based catalysts promoted with potassium and copper are used. One type of iron catalyst is used for the low-temperature Fischer – Tropsch (LTFT) processes used at SASOL I (i.e., ARGE and slurry phase processes) and another one in the high-temperature Fischer–Tropsch (HTFT) process, i.e., the Synthol Process used at Secunda and Mossel Bay in South Africa. A precipitated iron catalyst is used with the LTFT processes while a fused iron catalyst is used with the HTFT processes. Supported cobalt catalysts can also be considered for LTFT processes.

Fischer – Tropsch processes can be used to produce either a light synthetic crude oil (syncrude) and light olefins or heavy waxy hydrocarbons. The syncrude can be refined to environmentally friendly gasoline and diesel and the heavy hydrocarbons to specialty waxes or, if hydrocracked and/or isomerized, to produce excellent diesel fuel, lube oils, and a naphtha, which is an ideal feedstock for cracking to olefins. To give some idea of the flexibility of the potential product spectrum, the gasoline:diesel ratio may vary from 80 : 20 to 20 : 80. In addition, for a total of 50 % potential olefinic petrochemical feedstock, the light olefins (C_2 to C_4) can amount to 25 % of the products, a further 25 % of the product being in the form of olefins in the carbon number range C_5 to C_{10}. On the other hand, waxes can comprise more than 50 % of the total products.

For production of gasoline and light olefins, the FT process is operated at high temperature (330 – 350 °C), for production of waxes and/or diesel fuel, at low temperatures (220 – 250 °C). Traditionally the high-temperature FT process was performed in Synthol circulating fluidized bed (CFB) reactors and the low-temperature FT process in ARGE tubular fixed-bed (TFB) reactors. In the 1990s, much better reactor systems have been developed for both HTFT and LTFT processes. The conditions of both processes are compared in Table 5.

For HTFT the SASOL Advanced Synthol (SAS) reactor with solid – gas fluidization was developed. The SAS reactor gives very much

the same product spectrum as the CFB reactors, but much more effectively and cheaply.

Table 5. Process conditions for Fischer–Tropsch reactors

Parameter	LTFT	HTFT (SAS)
Temperature, °C	220–250	330–350
Pressure, MPa	2.5–4.5	2.5
$CO+H_2$ conversion, %	60–90	85

For LTFT, the SASOL Slurry Phase Distillate (SPD) reactor, of the bubble column type, was developed which is a significant improvement over the TFB reactor used in the ARGE process [61], [80]. In the Slurry Phase reactor products can be made with the same carbon chain length distribution as in the TFB reactor with Schulz–Flory distribution α-values of 0.95 and higher (for a definition of α-values see Section 2.2.1). The SPD reactor has a greater flexibility with respect to product distribution than the TFB reactor.

The heavy hydrocarbons from the SASOL SPD process are hydrogenated and converted to specialty waxes. Alternatively these waxy hydrocarbons can be very easily hydrocracked to excellent diesel fuel with a cetane number > 70 and negligible aromatics and zero sulfur content. At 780 kg/m^3 its density is somewhat lower than that of conventional diesel. If hydroisomerized, the waxy hydrocarbons can be used to produce lube oils.

The primary product spectra of the HTFT process are discussed in more detail in Section 2.2.2. The olefins from SASOL's HTFT plants are recovered commercially and ethylene, propene, 1-hexene, and 1-octene are produced more cheaply than from crude oil. The production of butenes, heptenes, and higher olefins in a HTFT plant is also being considered.

Low-Temperature Fischer–Tropsch Reactors. The two types of LTFT reactors are described below [81].

Tubular Fixed-Bed Reactor. The tubular fixed-bed reactor which has been operated by SASOL (using an iron catalyst) since 1953 and by Shell in Bintulu, Malaysia (using a supported cobalt catalyst) since 1993, makes use of tubes into which the catalyst is paced. Syngas is passed downward through the catalyst bed and is catalytically converted to hydrocarbons. The heat evolved is removed through the tube walls to produce steam on the shell side of the TFB reactor.

Slurry Bed Reactor. The slurry bed reactor which was successfully developed and operated by SASOL commercially since 1993, consists of a vessel containing a slurry of process-derived wax with catalyst dispersed in it. Syngas is bubbled through this slurry bed and is converted to hydrocarbons. The heat generated is passed from the slurry to the cooling coils inside the reactor to generate steam.

The light hydrocarbons, which are in the vapor phase, are removed from the freeboard at the top of the SSPD reactor with the unconverted reactants and are condensed in the downstream condensing train. The heavier liquid hydrocarbons are mixed into the slurry from which they are removed in a proprietary solid separation process developed by SASOL. Excellent results are obtained by this separation step.

The conventional TFB ARGE reactor and the state of the art slurry phase reactor are shown in Figure 3. The maximum capacity for a slurry phase reactor is an order of magnitude higher than that of the TFB reactor. The slurry phase reactor is much simpler in construction than the TFB reactor. The suspended cooling coils and a gas distributor give a much cheaper arrangement than the tube and tube sheet arrangement in the TFB reactor. Because of this, the slurry phase reactor lends itself much better to scale-up. At high gas throughputs, the TFB reactor becomes very complex and mechanically difficult to manufacture and the pressure drops across the tubes become excessive. The pressure drop across the TFB reactor varies from 0.3–0.7 MPa, depending on operating pressure, whereas it is typically less than 0.2 MPa across the slurry phase reactor. These differences make it possible to design (at present operating pressures of 2.5 MPa) single slurry phase reactors with capacities of 3000 m^3/d.

The most significant advantage of the slurry phase reactor is that it is well mixed and can be operated isothermally. The absence of axial and radial temperature gradients as in a TFB reactor, allows much higher average operating temperatures in the slurry phase reactor and hence higher reaction rates. Together with the more effective contact between the syngas and the catalyst particles, this leads to higher production rates for the same overall reactor dimensions even though

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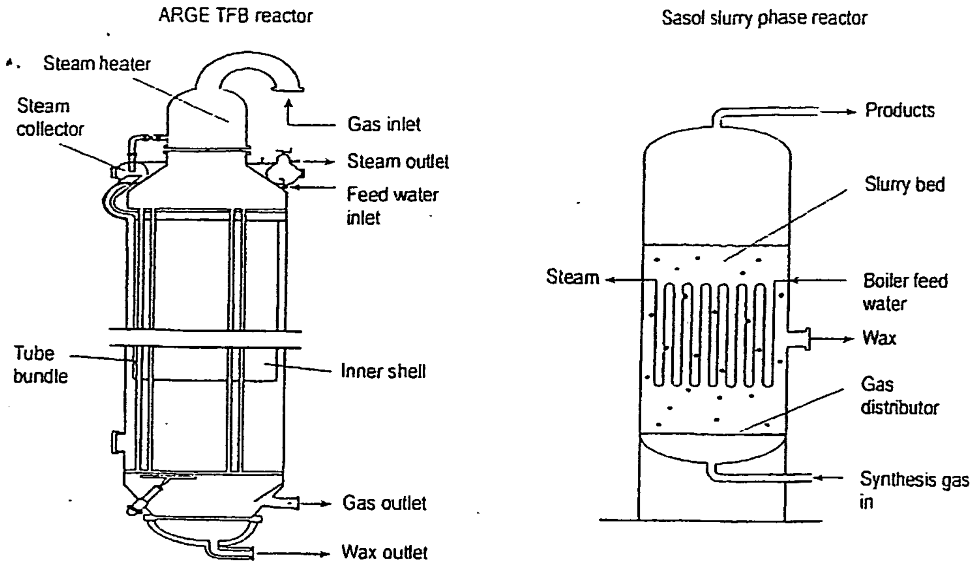


Figure 3. SASOL reactor system for LTFT

the catalyst inventory in the slurry phase reactor is lower than in the TFB reactor. Because all the catalyst particles are flexibly mixed with the slurry at more optimal process and conditions, the yields per reactor volume are higher and the catalyst consumption per ton of product is only 20 to 30 % of that of the TFB reactor. Because of the isothermal nature of the reactor, the easier control of average catalyst life, and the much smaller pressure drops across the reactor, the control of the reactor is much simpler and operating costs are significantly reduced.

High-Temperature Fluidized Bed Reactors. Also two types of HTFT reactors exist, which are described below.

Circulating Fluidized-Bed Reactor. Three Synthol CFB reactors were used commercially by SASOL from 1955 and another sixteen from the early 1980s on. For this type of reactor, fused iron catalyst is circulated with synthesis gas through a complex reactor – hopper – standpipe system and heat is removed as steam through coils suspended in the reactor section. The reactor system is complex and needs a complex support system to cope with the circulating catalyst loads and temperature differences which makes it expensive. The large tonnages of catalyst circulated cause relatively high pressure drops across the reactor system. These and other disadvantages are eliminated when using a SAS reactor which makes use of conventional solid – gas fluidization.

SAS Reactor. The Synthol CFB and SAS reactors are shown in Figure 4. The SAS reactor is a vessel containing a fluidized bed consisting of fused and reduced iron catalyst. Syngas is bubbled by means of a gas distributor through the bed where it is catalytically converted to hydrocarbons which at the process conditions of about 340 °C and 2.5 MPa, are in the vapor phase. The products and unconverted gases leave the reactor through internal cyclones. The SAS reactor is operated such that the cyclones can retain the catalyst so effectively that, in contrast to the CFB reactors, scrubber towers are not needed to remove the last traces of catalyst before the product stream is passed to the condensing train.

The major advantages of the SAS reactor over the CFB reactor are its simplicity, ease of operation, lower operating cost due to elimination of the catalyst recycle and lower maintenance, and in general higher conversions at higher gas loads. The latter together with the fact that more cooling coils can be installed in the SAS reactor and more heat can be removed, allows for larger capacity equipment which translates into advantages of economy of scale. Maximum capacities

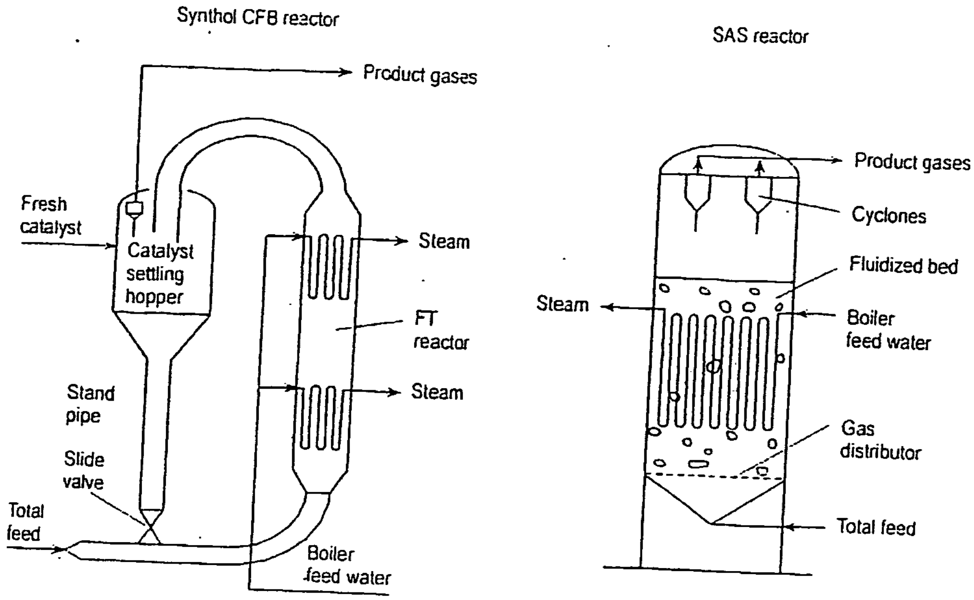


Figure 4. SASOL reactor system for HTFT

of 3200 m^3/d per reactor have been installed at the Secunda site.

2.2.1. Mechanisms

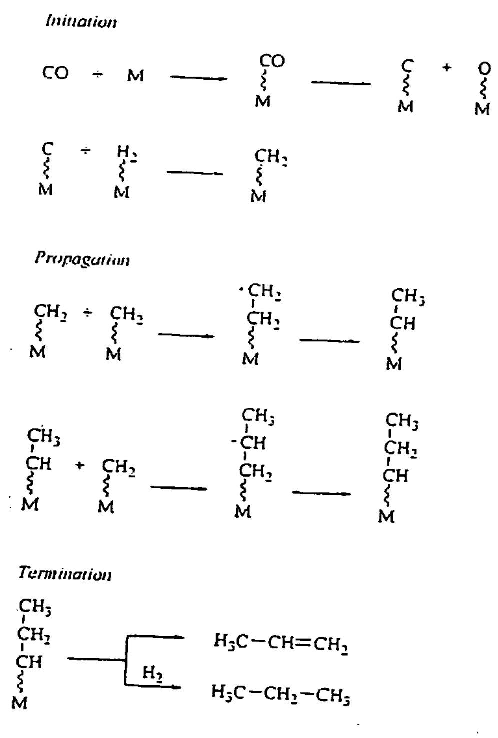
The mechanism of the Fischer–Tropsch synthesis is uncertain, but three theories have been developed [57], [82], [83].

In the first, the carbon monoxide dissociates at the catalyst surface (M) to carbon and oxygen atoms. Chemisorbed hydrogen reacts with the carbon to form CH_x entities, which combine into hydrocarbon chains. Chain termination produces α-olefins or alkanes (see reaction scheme 1). To account for the formation of oxygen compounds, a parallel mechanism postulates their production on oxide components of the catalyst surface [83].

In the second theory, carbon monoxide does not dissociate, but is hydrogenated to form oxymethylene species, which condense on the catalyst surface to propagate the hydrocarbon chain (reaction scheme 2).

In the third theory, the CO molecule does not dissociate, but inserts in an M–H or an M–C bond (reaction scheme 3) [84].

Reaction scheme 1



⌇ denotes a surface bond of indefinite order

Table 6. Fischer – Tropsch product selectivities, wt %

Product	SASOL I		SASOL II and III	
	ARGE [79]	ARGE [87]	Synthol [57]	Synthol [68]
CH_4	2.0	5.0	10	11.0
C_2H_4	0.1	0.2	4	7.5
C_2H_6	1.8	2.4	4	7.5
C_3H_6	2.7	2.0	12	13.0
C_3H_8	1.7	2.8	2	13.0
C_4H_8	2.8	3.0	9	11.0
C_4H_{10}	1.7	2.2	2	11.0
C_5-C_{11}, gasoline	18.0	22.5	40	37.0
$C_{12}-C_{18}$, diesel	14	15.0	7	11.0
$C_{19}-C_{23}$	7	6.0	4	3.5
$C_{24}-C_{35}$, medium wax	20	17.0	4	3.5
C_{35}, hard wax	25	18.0	–	–
Nonacid chemicals	3	3.5	5	6.0
Acids	0.2	0.4	1	NA *
Total	100.0	100.0	100.0	100.0

* NA = not available.

This mechanism has been widely accepted because CO insertion is known to occur with homogeneous catalysts [57]; however, the evidence is inconclusive for heterogeneous systems. A generalized mechanism that incorporates all three of these schemes has been proposed [59] (see nextpage).

Table 7. Product selectivities (carbon basis) for SASOL reactors, wt %[85]

Product	LTFT	SAS
Methane	4	7
C_2-C_4 olefins	4	24
C_2-C_4 paraffins	4	6
Gasoline	18	36
Middle distillates	19	12
Heavy cut and waxes	48	9
Water soluble oxygenates	3	6
Breakdown of the main oxygenate components for the SAS reactor (mass %)		
Main nonacid chemicals		
Acetaldehyde		3
Acetone		10
Ethanol		55
Methyl ethyl ketone		3
Isopropanol		3
n-Propanol		13
Isobutanol		3
n-Butanol		4
Acids		
Acetic acid		70
Propionic acid		16
Butyric acid		9
Valeric acid and higher		5

2.2.2. Product Selectivity and Characteristics

The ARGE fixed-bed reactor operates at relatively low temperature and is intended to produce a large quantity of wax and a minimum of methane. The objective of the Synthol reactor, on the other hand, is to maximize production of materials in the boiling range of gasoline. As mentioned previously, formation of waxy material must be avoided or catalyst particles stick together, resulting in bed defluidization. Product selectivities obtained with the SASOL fixed-bed ARGE system and Synthol reactors are shown in Tables 6 and 7. The two sets of data for the ARGE system probably represent different catalyst ages.

Table 8 shows the typical product composition for LTFT and HTFT reactors with iron catalyst [85].

Because of the higher operating temperature, Synthol gasoline contains less paraffinic and more olefinic, aromatic, and oxygenated components than ARGE gasoline. The latter has a high percentage of *n*-alkanes and a low research octane number (RON) of 35, but the diesel has a high cetane number of 75. Synthol gasoline, with its high olefinic and some aromatic content, has a higher RON of 65, but an octane number that is low for gasoline. The Synthol diesel fuel has a cetane number of 55.

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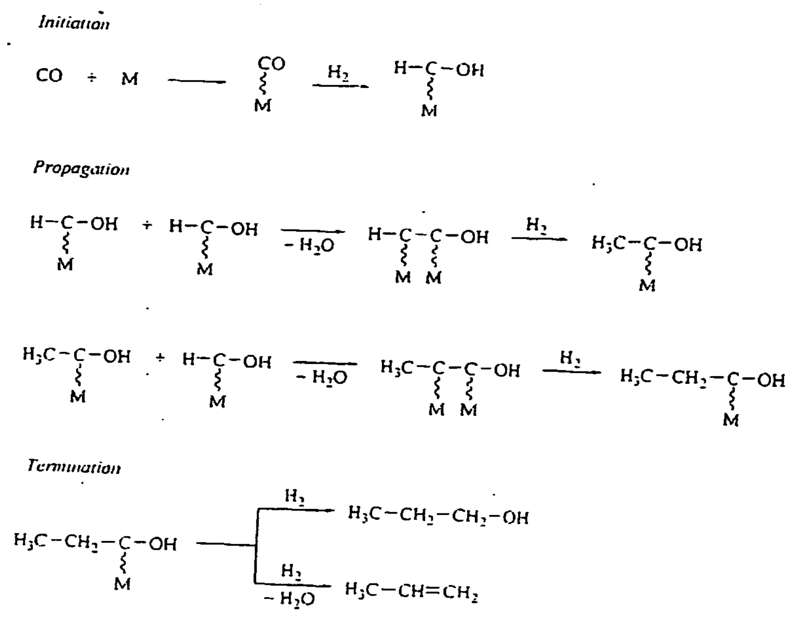
Reaction scheme 2



⌇ denotes surface bond of indefinite order

Reaction scheme 3

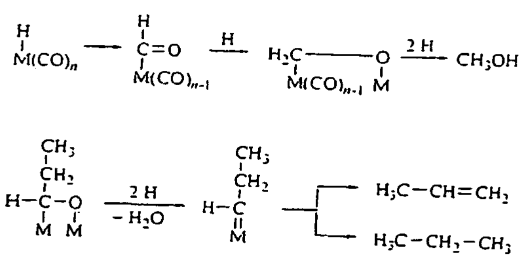


Table 8. Typical product compositions for LTFT and HTFT reactors (with iron catalyst) [85]

	TFB reactor		SSPD reactor		HTFT	
	C_5-C_{12}	$C_{13}-C_{18}$	C_5-C_{12}	$C_{13}-C_{18}$	C_5-C_{10}	$C_{11}-C_{14}$
Paraffins, %	53	65	29	44	13	15
Olefins, %	40	28	64	50	70	60
Aromatics, %	0	0	0	0	5	15
Oxygenates, %	7	7	7	6	12	10
n-Paraffins, %	95	99	96	95	55	60

The C_3 Synthol hydrocarbons are 86 % olefinic, compared to 60 % for those from the ARGE process. For the C_4 hydrocarbons, the corresponding figures are 82 % and 56 %. The high percentage of C_3 and C_4 olefins is a great advantage, because these olefins produce more gasoline by catalytic polymerization and alkylation.

The selectivities obtained in the SAS reactors are very similar to those in the Synthol CFB reactors because both processes use a catalyst with the same composition. A slightly lower methane selectivity can be attained in the SAS reactor because it is operated more isothermally.

The Slurry Phase Distillate process is designed to produce predominantly middle distillate fuels such as gasoline or diesel. At the same time a small amount of naphtha is manufactured as coproduct. These fuels are compatible with existing petroleum derived fuels, and thus no engine modifications or special distribution infrastructure are necessary [86]. At the same time, this synthetic diesel has several environmental advantages over conventional fuels. It has superior combustion characteristics due to its high cetane number (> 70), and is free of sulfur and aromatic compounds (see Table 9).

Environmental concerns have already led to specifications on fuels being tightened in several regions. This is expected to continue, resulting in more stringent specifications in the future. Some refiners may face difficulties in meeting these specifications due to either equipment or feedstock limitations. The environmental advantages of the synthetic product will in this case result in synthetic diesel selling at a premium rate compared with conventional diesel (expected at $ 2.4/bbl premium) for use as a blending component.

Table 9. Comparison of the quality for diesel fractions [86]

	SPD process	Conventional
Sulfur	< 10 ppm	500 ppm
Aromatics	< 1 %	10–25 %
Cetane number	> 70	45

The emissions from diesel engines operating on standard, "reformulated", and Fischer–Tropsch diesel fuels have been measured by the South West Research Institute, a large independent fuels and lubricants testing organization in the USA (see Table 10). These tests showed that Fischer–Tropsch diesel results in reduced exhaust emissions (particulates, nitrogen oxides, carbon monoxide, and unburned hydrocarbons) compared to both the standard and the "reformulated"diesels [86].

Table 10. Comparison of Fischer–Tropsch diesel in SWRI diesel engine emission tests [86]

Reduction in	Average diesel	Reformulated diesel
Hydrocarbons	33 %	20 %
CO	46 %	36 %
NO_x	8 %	4 %
Particulates	30 %	26 %

The coproduction of some chemicals is possible with the Slurry Phase Distillate process. The products are primarily a mixture of linear paraffins and olefins, with a wide range of carbon chain lengths. It is feasible to recover linear paraffins that can be used for the manufacture of detergent alkylates and other chemical uses. The separation of linear olefins for the production of detergent feedstock, and the production of lubricating oil base stocks, are also possible. The recovery of these fractions is economically justified for a large scale facility consisting of several modules, as these cuts form only a small fraction of the overall production [86].

2.2.3. Catalytic Selectivity

Fischer–Tropsch processes include catalytic carbon–carbon and carbon–hydrogen bond formation and carbon–oxygen bond rupture [82]. Whatever the mechanisms, the resulting hydrocarbon chain distribution can be explained by a polymerization process, adding one carbon atom at a time to the growing alkyl chain. At any point in the chain, growth can be terminated by hydrogen atom addition or by α-hydrogen abstraction, followed by desorption from the catalyst surface. This process results in a distribution of chain lengths, as in all polymerization processes. Product distribution can be predicted accordingly. The Schulz–Flory distribution can be used to predict selectivity, assuming that all hydrocarbon species on the catalyst surface, regardless of chain length, add a carbon atom with equal probability to produce a chain that is one unit longer [88], [89]. For a hydrocarbon chain having n carbon atoms, the probability of poly-

merization at the first carbon and at each successive carbon is α; the probability that polymerization does not occur at the final carbon atom is $(1-\alpha)$. Thus, the probability that the hydrocarbon chain is composed of n carbon atoms is:

$$P_n = \alpha^{n-1}(1-\alpha)$$

Therefore, P_n is equivalent to the mole fraction of the nth oligomer. If the assumption is made that the molecular mass of the monomer is the same, independent of position, the mass fraction (W_n) is simply the mole fraction multiplied by the chain length n and divided by $1(1-\alpha)$ (the average degree of polymerization). The equation becomes:

$$W_n = n\alpha^{n-1}(1-\alpha)^2$$

Rearranging and taking logarithms gives the Schulz – Flory equation:

$$\log\frac{W_n}{n} = n\log\alpha + \log\frac{(1-\alpha)^2}{\alpha}$$

When $\log\frac{W_n}{n}$ is plotted against n, a straight line of slope $= \log\alpha$ should be obtained if the Schulz – Flory polymerization mechanism is obeyed. With increasing α, the product contains higher molecular mass hydrocarbons. The chain growth probability distribution results in a broad Fischer – Tropsch product spectrum. In addition, only C_1 hydrocarbons can be produced with 100 % selectivity (i.e., when $\alpha = 0$). The Schulz – Flory distribution places a significant limitation on the maximum yield of the transportation fuel fraction. Selectivity as a function of α is shown in Figure 5 [57]. Chain growth is influenced by temperature, pressure, feed composition, and catalyst [55], [90], [91].

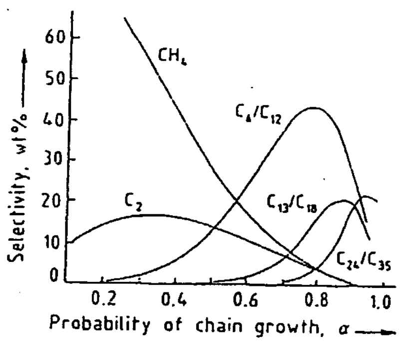


Figure 5. Calculated product selectivities from Schulz – Flory analysis

The SASOL operation uses a precipitated iron catalyst in the LTFT reactors (ARGE and Slurry Phase) and a fused iron catalyst in the HTFT Synthol reactors. The fixed-bed catalyst is activated with hydrogen under mild conditions to produce the large metallic surface area necessary for high activity [57]. Selectivity is apparently influenced by the activation or conditioning process. Copper increases the rate of iron oxide reduction and the activity of the catalyst, but not its selectivity for wax [57]. Synthesis gas converts the metallic iron in the partly reduced catalyst to a carbide form (Fe_5C_2) known as Hagg carbide [57]. Promoters, such as K_2O, increase α, i.e., selectivity for longer hydrocarbons, and production of acid. Catalytic activity passes through a maximum with increasing K_2O content. Among support materials for the precipitated iron catalyst, silica gives both the highest activity and the highest wax selectivity [57].

The Synthol catalyst is prepared from mill scale (waste iron) containing small amounts of impurities, such as SiO_2, TiO_2, MgO, and Al_2O_3. The catalyst and promoters are electrically fused into ingots, which are crushed to the necessary particle size and then reduced with hydrogen in fixed fluidized-bed reactors. The surface area increases according to the degree of reduction to a final value between 2 and 30 mg^2/g; pore volume also increases [57], [58]. Potassium is the most important promoter [59]. Structural promoters (Al_2O_3, MgO, and Cr_2O_3) increase and stabilize the surface [57].

Increased temperature in the Fischer – Tropsch synthesis reduces α and favors lower molecular mass products, the chemical characteristics of which also vary (see Tables 11 and 12) [57], [59].

Table 11. Influence of temperature on selectivity of Synthol catalysts [57], [59]

Temperature, °C	Methane selectivity,	Ratio $C_3H_6 : C_3H_8$	Aromatics in gasoline, wt %
310	10	11	4
330	14	10	8
350	17	9	10
360	20	8	13
370	23	6	18
380	28	4	26

Table 12. Influence of temperature on selectivity of ARGE catalysts [57], [59]

Temperature, °C	Wax selectivity, %	Olefins in diesel, wt %
213	47	45
227	34	39
237	24	33
247	17	40

Gas composition and pressure also influence catalyst selectivity [57], [59], probably because, at the catalyst surface, hydrogen favors chain termination and carbon monoxide favors chain propagation. This suggests a correlation between product selectivity and the ratio of hydrogen to carbon monoxide in the feed gas. Wax formation in the fixed-bed reactor is in fact correlated with the H_2 : CO ratio; lower values favor polymerization and higher values favor wax production (higher α). The total reactor pressure, however, has little or no effect on selectivity [59].

This correlation is not observed with the fluidized-bed Synthol catalyst system. At SASOL methane selectivity has been found to correlate with the function:

$$\frac{P_{H_2}^{0.5}}{(P_{CO}+P_{CO_2}+P_{H_2O})}$$

Sulfur poisoning decreases the activity of the Synthol catalyst but increases the formation of olefins and higher hydrocarbons [92]. The structure of the Synthol catalyst, under synthesis conditions, changes continuously from the freshly reduced catalyst to the fully mature catalyst [62]. The main reason for this change is carbon formation during the synthesis process. The change in morphology of the catalyst can affect the catalyst's product selectivity after low-level sulfur poisoning.

2.2.4. Refining of Crude Products

Crude Fischer–Tropsch products from Synthol and ARGE units require extensive refining for use as gasoline and diesel fuel (see Table 13).

Table 13. Refining of Fischer–Tropsch products

Refining process	Purpose
FT product fractionation	separation into light gases and feeds for polymerization and hydrotreating
FT product hydrotreating	saturation of olefins and destruction of alcohols and acids
Hydrotreated product fractionator	separation of hydrotreated products into pentane–hexane stream for isomerization, C_7–C_{11} for reforming, and diesel and fuel oil products
Catalytic reforming	aromatization to increase octane number of gasoline stream
C_5–C_6 Isomerization	isomerization of straight chains to increase octane number of hexanes and pentanes
Catalytic polymerization	polymerization of propene and butene to gasoline
Alkylation	catalytic alkylation of isobutane and unpolymerized C_3–C_4 olefins to increase gasoline yield
Polygas hydrogenation	saturation of olefins in heavy catalytic polygasoline
Alcohol recovery	preparation of marketable alcohol mixture
Wax hydrocracking	cracking of wax components into gasoline and diesel hydrocarbons

Figure 6 illustrates an indirect liquefaction plant producing transportation fuels. If only Synthol reactors are used, as at SASOL II and III, the wax hydrocracker is eliminated. Wax produced in ARGE units can be selectively cracked to C_1–C_4 hydrocarbon gases, gasoline, and diesel in the proportions 5 : 15 : 80 (by mass) [93]. SASOL II and III operations resemble those described in Table 13 [94] (see Section 2.2.6).

2.2.5. Integrated Plant Configurations

The flow sheet of an integrated indirect coal conversion plant, combining the steps discussed in previous sections, is shown in Figure 7. In the upper configuration, designated as the *mixed-output mode,* liquid transportation fuels and substitute natural gas (SNG) are produced. In the lower configuration, the *all-liquid-output mode,* the light hydrocarbon gases are autothermally reformed back to synthesis gas; the net output contains only C_3 and higher liquid hydrocarbons. The SASOL II and III operations are of this

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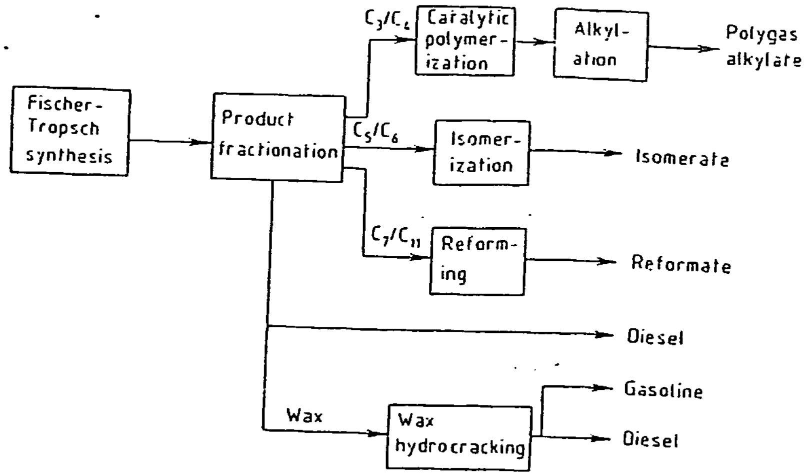

Figure 6. Flow sheet for Fischer – Tropsch products

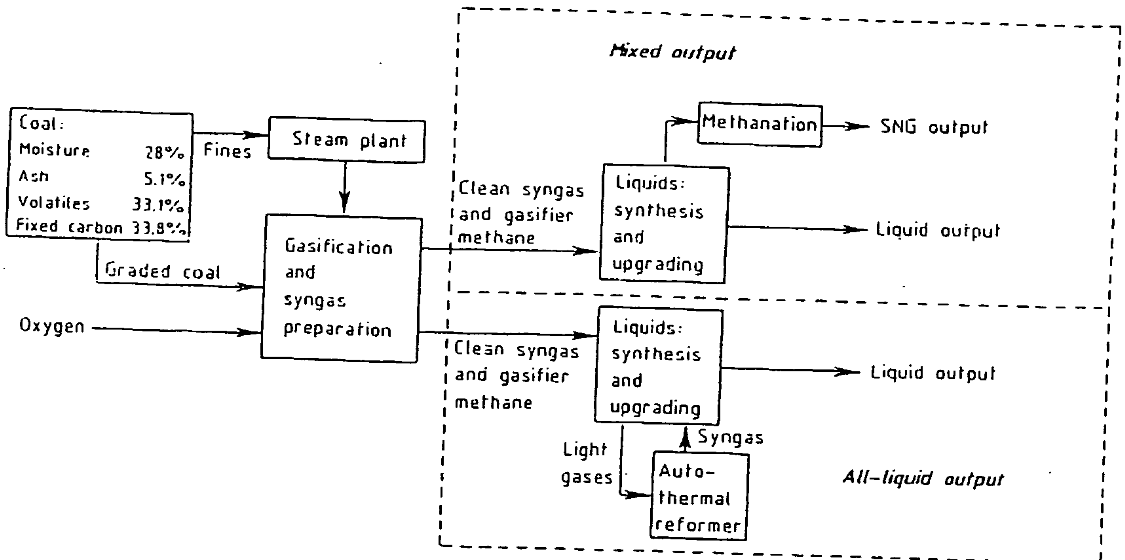

Figure 7. Flow sheet for integrated liquefaction

type. The flow sheet was adapted from studies conducted by Mobil Research and Development Corp. [71] and Mitre Corp. [70].

The plant represented in Figure 7 is designed to process 25 200 t/d of Wyoming subbituminous, noncaking reactive coal. To meet plant requirements, ca. 18 % of the coal is needed to produce high-quality steam, most of which is used for oxygen production for the gasification section. Fixed-bed, dry-bottom Lurgi gasifiers produce the synthesis gas, which is very wet, with a molar hydrogen : carbon monoxide ratio of ca. 2 : 1. After being quenched with water to remove tars and particulates, the synthesis gas is split into two streams. About 20 % is passed to shift reactors, where the hydrogen : carbon monoxide ratio is raised to 10 : 1. Recombination of the two streams gives an overall H_2 : CO ratio of 2.5 : 1, as required for Synthol reactors. The combined gas is purified by the Lurgi Rectisol process, passed to the Synthol units, and refined (see Section 2.2.4).

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Table 14. Calculated yields from model liquefaction plants

Products	Mixed output	All-liquid output
SNG, m^3/d (STP)	4.91×10^6	–
Gasoline, m^3/d	2160	4465
Propane, m^3/d	176	387
Butane, m^3/d	23	51
Diesel, m^3/d	324	807
Fuel oil, m^3/d	99	217
Alcohols, m^3/d	291	640
Annual thermal output (LHV *), GJ/a	85 627 000	65 418 000
Liquid yield, m^3 C_3^+/t dry coal	0.159	0.334
Overall efficiency (LHV *), %	54	41
Total plant coal (LHV *), GJ/a	158 424 000	158 424 000

* LHV = lower heating value.

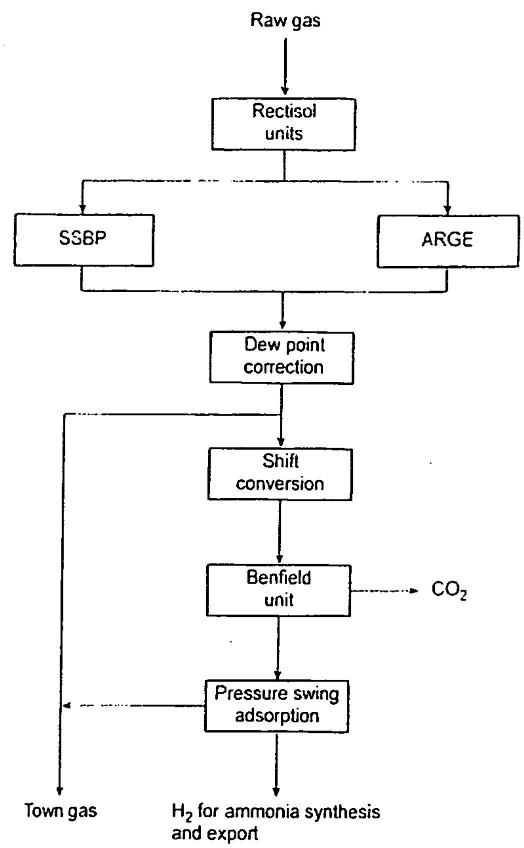

Figure 8. Flow sheet for SASOL I synthesis

The gasification process includes auxiliary units for gas – liquid separation and recovery of phenol, sulfur, and ammonia. These units contribute to pollution control (see Section 2.5).

Off-site units are required for oxygen production, steam boilers and superheaters, stack gas precipitation and flue gas desulfurization, coal handling and preparation, ash removal, water supply for boilers and cooling towers, power generation, wastewater treatment, storage, fuel blending, and catalyst preparation.

The calculated yields based on a model commercial plant for mixed-output and all-liquid operation are given in Table 14. In the mixed-output mode, 65 % of the thermal output is in the form of SNG, which originates from the Lurgi gasifier and also from the Synthol reactor. In the all-liquid mode, the methane and ethane are reformed and resynthesized to liquids, reducing overall plant efficiency from 54 to 41 %. Overall plant efficiency is defined as the LHV energy content of all the products divided by the LHV energy content of the total feed coal.

Energy relations in the all-liquid mode as a percent of total plant coal input energy (LHV) are as follows:

Input coal	100 %
Gasifier output	74 %
Synthesis gas	63 %
Clean gas	62 %
Raw products	45 %
Refined products	41 %

The raw gasifier output represents ca. 74 % of the energy of the total feed coal and includes the tars, oils, and phenols recovered from the wash and wastewaters. A calculation based only on gases produced would reduce the efficiency to ca. 65 %. After the shift and cleaning steps, the energy remaining in the gas represents 62 % of the total input coal. In the all-liquid mode, the methane and ethane are reformed to synthesis gas with a loss of energy; thus, the crude products represent only ca. 45 % of the input coal energy. Refining to final products lowers this value to 41 %.

2.2.6. Commercial Practice at SASOL

The SASOL plants, in operation in South Africa since 1956, are the only indirect coal liquefaction plants in the world that currently produce liquid transportation fuels by the Fischer – Tropsch synthesis. The original Sasol-

burg site has been converted entirely to produce products other than liquid transportation fuels, mainly waxes, paraffins, ammonia, and town gas (see Fig. 8).

The Secunda site consists of two identical plants previously called SASOL II and SASOL III but now referred to as SASOL West and SASOL East. These plants are virtually identical and they now also produce a wide range of petrochemical products and a methane-rich pipeline gas.

There are 36 gasifiers at each plant (72 in total at Secunda). The Mark-IV Lurgi dry-ash gasifiers used have 3.85 m internal diameter. They were originally designed to produce ca. 55 000 m^3/h (STP) of dry raw gas [59], but are now capable of producing about 85 000 m^3/h. The raw gas from these gasifiers is cooled in waste-heat boilers and washed with water. Particulates, ammonia, tars, oils, and phenols are removed. The cooled, stripped gas, still containing hydrogen sulfide and carbon dioxide, is purified by a chilled methanol wash in Rectisol units, leaving less than 40 ppb (by volume) of H_2S and less than 1 % CO_2.

The product work-up system used for the Secunda plants is shown in Figure 9. The tail gas from the separator is scrubbed to remove carbon dioxide and then fractionated in a cryogenic unit. The recovered ethylene from this cryogenic unit is a valuable chemical feedstock [59]. Some pipeline or town gas is withdrawn from the methane-rich product stream from the cryogenic unit and the remainder is autothermally reformed to synthesis gas and recycled. The propene was originally polymerized to either gasoline or diesel in a catalytic unit that can also accept butene as a feedstock if higher diesel yields are desired. Nowadays the propene is mostly recovered as a valuable petrochemical feedstock and the butene is processed to gasoline in an alkylation unit.

As shown in Figure 9, pentane and hexane are isomerized and the $C_7 - C_{11}$ hydrocarbons are reformed over a platinum catalyst to increase the octane rating of the gasoline. Higher carbon number fractions are catalytically hydrodewaxed and marketed as a zero sulfur diesel fuel [94]. Increasingly α-olefins such as 1-hexene and 1-octene are being recovered as petrochemical feedstocks.

2.2.7. New and Developing Technologies

The conventional fluidized-bed reactor concept has been developed and scaled-up by SASOL to the limits of this technology at the Secunda site in South Africa. This type of reactor was first operated at the Hydrocol plant in Brownsville, Texas in the early 1950s. The tubular fixed-bed reactor concept used in Germany in the early applications (maximum production in 1944) has now been developed further and scaled up by Shell to the limits of this technology for the commercial plant in Bintulu, Malaysia.

The slurry phase or slurry bubble column reactor (the successor to the TFB reactor for LTFT) is potentially the best reactor choice for the Fischer–Tropsch synthesis and it has yet to be developed to its full potential in a commercial application. This type of reactor was first applied in a demonstration unit at Rheinpreussen, Germany, in the 1950s using an iron-based catalyst for the production of gasoline. SASOL, Statoil, Exxon, Shell, and more recently, IFP/AGIP have been working on the concept of using a supported cobalt catalyst with this type of reactor. SASOL and Exxon have operated demonstration-scale reactors, and Shell and Air Products have participated in demonstration scale tests using the US DOE facilities at La Porte, Texas. The concept is to produce wax as the main primary product from the reactor which also produces straight-run diesel and naphtha and optionally kerosene and liquefied petroleum gas (LPG). Only SASOL has operated a commercial-scale slurry phase reactor. The characteristics of the Rheinpreussen plant were as follows [95]:

Reactor dimensions	155 cm diameter 8.6 m height
Slurry volume	10 000 L
Catalyst, Fe	800 kg
Production output	11.5 t/d
Average temperature	268 °C
Pressure	1.2 MPa
Feed gas rate at STP	2700 m^3/h
Hourly space velocity of gas	270 L of gas per liter of expanded slurry
Carbon monoxide conversion	91 mol %
Overall syngas conversion	89 mol %
Syngas feed ratio H_2 : CO	0.67
Linear velocity of syngas	9.5 cm/s
Catalyst composition:	
Fe	1000 g/kg
Cu	1 g/kg
K_2O	0.5 – 5 g/kg

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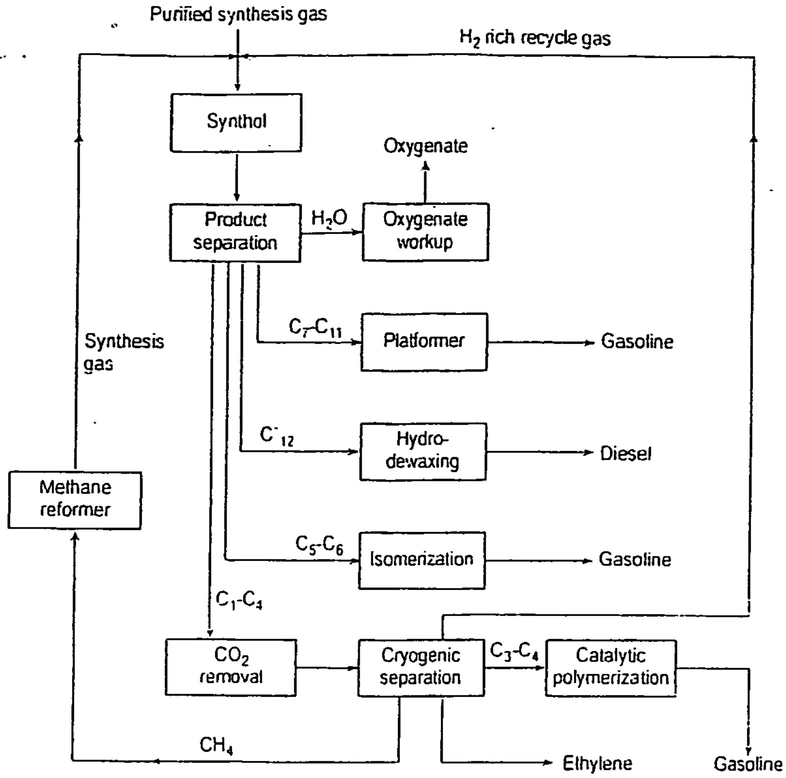

Figure 9. Flow sheet for SASOL II products workup

The height of the expanded liquid-catalyst bed was kept constant by adding melted wax or by withdrawing the products with a high boiling point through a pressure filter to remove the catalyst. The product distribution (in wt %) obtained from the operating plant at maximum gasoline production was as follows:

Methane and ethane	3.2
Ethylene	3.6
Propene	18.0
Propane	4.5
Butene	3.8
Butane	1.3
Boiling range	
40–180 °C	53.6
180–220 °C	4.0
220–320 °C	6.0
>320 °C	1.9

High selectivity for gasoline was achieved, almost 54 % compared to the 48 % predicted from probability considerations. If propene and butene polymerization was included, gasoline production reached 73 % compared to 62 % for Synthol gasoline. Attempts to repeat these results have been unsuccessful [97–100].

In a later investigation at Mobil, slurry-phase Fischer–Tropsch synthesis was combined with fixed-bed zeolite processing of the crude products [101]. Processing of such products over zeolite ZSM-5 was known to form high-octane gasoline by a combination of isomerization, aromatization, alkylation, and elimination of oxygen compounds [102].

In the first stage of the *Mobil two-stage process*, the Fischer–Tropsch synthesis was carried out in a slurry reactor containing alkaline-promoted iron catalysts in a liquid heat transfer medium. Product selectivities were as follows [101–103]:

Reactor conditions	
Pressure	1.48 MPa
Temperature	260 °C
H_2 : CO Molar ratio	0.68
Hourly space velocity at STP, L/g Fe catalyst	2.6
Conversion data, mol %	
Hydrogen	79
Carbon monoxide	92
Syngas	87
Selectivities, wt %	
CH_4	6.8
C_2H_4	1.6
C_2H_6	2.8
C_3H_6	7.5
C_3H_8	1.8
C_4H_8	6.2
C_4H_{10}	1.8
C_5-C_{11}	18.6
Light hydrocarbons	14.3
Heavy hydrocarbons	27.6
Wax	10.0

When the reactor was operated at low C_1 and C_2 yields (ca. 5 wt %), large quantities of wax (C_{23} +) were produced; this wax was removed to prevent excess liquid buildup. the catalyst was returned to the reactor without deactivation, which may be difficult in a commercial operation. The effect of the zeolite second stage is shown in Table 15.

Table 15. Selectivities before and after ZSM-5 reactor

Products	First stage, wt %	Second stage, wt %
C_1	6.5	6.8
C_2*/C_2**	1.7/2.7	1.0/2.9
C_3*/C_3**	7.1/1.9	2.0/5.6
C_4	5.9	4.7
Iso-C_4 /n-C_4	0/1.8	6.6/6.1
C_5-C_{11}	27.1	51.5
C_{12}+ (liquid)	33.3	0.8
Reactor wax	12	12
C_5-C_{11}, wt %		
Alkanes	–	49.4
Olefins	–	22.8
Naphthenes	–	4.5
Aromatics	–	23.3

* Saturated.
** Unsaturated.

Research on the Fischer–Tropsch process is continuing at SASOL and elsewhere. Much of this work is aimed at improving selectivity by developing novel catalysts and reactors. SASOL has developed high-activity, long-life, supported cobalt catalysts, that have a longer service life and higher activity than the conventional iron-based catalysts [85]. This more than compensates for the higher raw material costs. However, further work on improving the life of the iron-based catalyst in slurry phase reactors may still result in the use of iron catalyst with low H_2 : CO ratio syngas derived from coal. The iron catalyst exhibits water–gas shift activity which is absent from cobalt-based catalysts. Water–gas shift activity is desirable for low H_2 : CO ratio coal-derived syngas but not for the higher H_2 : CO ratio natural gas-derived syngas.

The selective hydrocracking of Fischer–Tropsch waxes yields 80 % diesel fuel (cetane number ca 70), 17 % naphtha, and 3 % C_1-C_4 hydrocarbon gases. The wax is an ideal hydrocracker feedstock because it contains no aromatic, nitrogen, or sulfur compounds. When combined with the straight-run products (which are typically hydrotreated to remove olefins and oxygenates) the final diesel : naphtha ratio is typically 75 : 25. There is considerable flexibility for the processing of the wax. It may be fed to a Fluidized Catalytic Cracking (FCC) unit to produce gasoline; it may be fractionated and hydroisomerized to produce lubricant base oils, or intermediate severity hydrocracking/hydroisomerization may produce a combination of FCC feedstock, lubricants, diesel fuel, and naphtha. A kerosene or jet fuel product intermediate between diesel and naphtha may also be produced. The naphtha is an ideal feedstock for cracking to olefins since it is completely paraffinic [96].

2.2.8. Advanced Systems

Integrated indirect liquefaction by SASOL technology with two modes of operation was discussed in Section 2.2.5. In the mixed-output mode, gas and liquid fuels are produced together. In the all-liquid-output mode, the C_1 and C_2 hydrocarbons are reformed to synthesis gas and only liquid fuels are produced. The expected effect of using advanced entrained gasification, such as the Shell system, in place of the dry-ash Lurgi is significant, with an increase in net efficiency of ca. 23 % [104]. This would result in a 23 % reduction in gasoline cost if commercial operation matches pilot-plant results.

Predicting the effect of the slurry-phase system and the Mobil two-stage slurry ZSM-5 system is more difficult. However, if the Rheinpreussen-Koppers pilot plant results could

be scaled up, the plant efficiency of a Shell gasification system would increase by an estimated additional 10 % [104].

2.3. Methanol and Methanol to Gasoline (MTG)

Methanol formation can be seen as a variant of the Fischer – Tropsch synthesis:

$$CO + 2\,H_2 \longrightarrow CH_3OH \quad \Delta H_{298} = -90.84\ \text{kJ/mol}$$

$$CO_2 + 3\,H_2 \longrightarrow CH_3OH + H_2O \quad \Delta H_{298} = -49.57\ \text{kJ/mol}$$

Both reactions are exothermic and proceed with volume contraction; they are consequently favored by a low temperature and high pressure.

Both high- and low-pressure processes are available to hydrogenate carbon monoxide. The *high-pressure method* was commercialized by BASF in 1923 [105] and dominated the market in various versions until 1966 [106]. These processes used a zinc – chromium oxide catalyst at or above 340 °C and required a pressure of 30 – 50 MPa to obtain methanol concentrations of ca. 5 – 6 vol % in the effluent gases from the reactor, together with significant amounts of methane, dimethyl ether, ethanol, and higher alcohols.

In 1966 ICI introduced a *low-pressure methanol synthesis* that used a copper – zinc – chromium catalyst at 5 MPa [105]. Other low-pressure processes were developed later by Lurgi Kohle & Mineralöltechnik [107], Mitsubishi Gas & Chemical Co., and Haldor Topsøe [108]. These processes differ primarily in operating pressure, catalyst, and reactor design, especially with respect to heat recovery and temperature control. The ICI and Lurgi processes are dominant.

In the *ICI methanol process,* sulfur-free synthesis gas is mixed with part of the recycle gas, heated, and fed to the converter at 5 – 10 MPa. The remainder of the recycle is used as quench gas and is admitted to the catalyst bed through a series of lozenge-shaped distributors. In the reactor, the CO, CO_2, and H_2 are partially converted to methanol. The hot exit gases are cooled to condense the methanol. Part of the unreacted gases is purged to prevent inert impurities from accumulating; the remainder is compressed and recycled to the reactor. The typical recycle ratio ranges from 5 at 10 MPa to 8 at 5 MPa [108]. Conversion of CO to methanol per pass is normally 16 – 20 %. Feed-gas composition is typically 59 vol % H_2 and 27 vol % CO, to give an $H_2 : CO$ ratio of 2.17.

The ICI process uses a hot-wall, catalytic, fixed-bed, vapor phase, adiabatic reactor designed for rapid catalyst loading and unloading and for efficient mixing of cold and hot gases. The reactor holds a bed of catalyst with quench gas distributors at several levels to control temperature. The bottom catalyst layer is usually kept at ca. 230 °C. Catalyst lifetime is typically 2 – 3 years.

The *Lurgi process* uses a tubular reactor with copper – zinc catalyst packed in vertical tubes that are contained within a reactor shell filled with boiling water. This closely resembles the ARGE Fischer – Tropsch reactor; it differs from the ICI methanol system in having only one feed location. Hot synthesis gas is fed to the top of the reactor and distributed uniformly through the tubes. The heat of reaction is removed by the circulating boiling water [107].

The U.S. Department of Energy (DOE) and the Electrical Power Research Institute (EPRI) have supported research on methanol synthesis by a novel system known as *liquid-phase methanol* (LPM), in which synthesis gas reacts with a catalyst suspended in a liquid heat transfer medium. This reactor resembles a slurry reactor (Section 2.2.7) except for the circulation through an external heat-transfer loop attached to the reactor. The experimental LPM reactor at LaPorte, Texas, is 57 cm in diameter and 5.5 m high [109].

Mobil methanol-to-gasoline process. Methanol can be used as a fuel alone or blended with gasoline. In addition, it can be converted to gasoline by the Mobil MTG process [110]. Methanol as the first stage in the indirect liquefaction affords 100 % selectivity for gasoline, much higher than that obtainable in the Fischer–Tropsch synthesis with its wide range of hydrocarbon products.

In the Mobil MTG process, methanol is dehydrated over the zeolite ZSM-5 catalyst [111], first to dimethyl ether and then to hydrocarbons that are predominantly in the gasoline boiling range, with some LPG and fuel gas [68]. The reaction exotherm ranges from 1.5 to 1.75 kJ/g

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methanol, depending on the product distribution [68]. The complex reaction sequence can be represented as follows [68]:

$$2\,CH_3OH \longrightarrow (CH_3)_2O + H_2O$$

$$(CH_3)_2O \longrightarrow (CH_2)_2 + H_2O$$

$$\text{Light olefins} \longrightarrow \text{Heavier olefins}$$

$$\text{Heavy olefins} \longrightarrow \text{Aromatics, alkanes, cycloalkanes}$$

For 100 g of methanol consumed, the stoichiometric yields are 43.75 g of hydrocarbons and 56.25 g of water.

Mobil has developed two reactor configurations: the adiabatic fixed-bed and the fluidized-bed processes. In the *adiabatic fixed-bed process*, two reactors are used in series, the first for dehydrating methanol to an equilibrium mixture of dimethyl ether and water. This mixture is combined with recycle gas from the second reactor and converted to hydrocarbons and water over the zeolite catalyst. The recycle gas, which consists of light hydrocarbons, aids in heat removal from the second stage [68]. The catalyst in the MTG reactor requires regeneration about every 20 d.

Much of the development work has been performed in a 0.64 m^3/d pilot plant at Mobil's New Jersey facility. The dehydration reactor is 5 cm in diameter by 4 m and the conversion reactor is 10 cm in diameter by 4 m. In 1980, the government of New Zealand decided to use this technology in a 2700 m^3/d plant for converting natural gas to gasoline [112].

Development of the *fluidized-bed MTG process* was partially supported by the U.S. DOE. A 0.64 m^3/d pilot plant was operated successfully, demonstrating the following advantages over the fixed-bed process [110]: heat removal at high temperature and mixing of catalyst and reactants are highly efficient, high catalyst activity is maintained with continuous regeneration, and the heat of reaction is utilized to vaporize feed methanol.

Table 16. MTG operations [68], [110]

	Fixed-bed	Fluidized-bed	
	0.64 m^3/d	0.64 m^3/d	16 m^3/d
MTG inlet temp., °C	360	413	407
outlet temp., °C	412	413	407
Gas recycle ratio (molar)	9	0	0
Weight hourly space velocity, (pure methanol)	1.6	1.0	1.1
Reactor pressure, MPa	2.17	0.27	0.41
Product, wt % [a]			
Hydrocarbons	43.7	43.5	40.0
Water	56.2	56.0	NA [b]
CO, CO_2, H_2, other	0.1	0.5	NA
Hydrocarbon product, wt %			
$C_1 + C_2$	2.1	5.6	NA
Propane	8.6	5.9	NA
Propene	0.2	5.0	NA
n-Butane	4.2	1.7	NA
Isobutane	8.4	14.5	NA
Butenes	0.7	7.3	NA
C_5+ gasoline	75.8	60.0	NA
Gasoline yield, wt % hydrocarbons [c]	80.2	88.0	89.0
Research octane number [d]	95	96	95

[a] Based on methanol feed.
[b] NA = not available.
[c] Includes alkylate.
[d] Unleaded product.

The 0.64 m^3/d pilot plant's reactor is 10 cm in diameter and 7.6 m high, with provision for external catalyst circulation and regeneration [113]. In 1980, an international project was initiated to construct and operate the fluidized-bed MTG process on a 16 m^3/d demonstration scale at Wesseling, Federal Republic of Germany. Participants included Mobil, Uhde, and Union Rheinische Braunkohlen Kraftstoff (URBK). Financial assistance was also provided by the U.S. DOE and the Ministry for Research and Technology (BMFT) of the Federal Republic of Germany [110]. The conversion rate has averaged 850 kg/h of methanol, and the plant has met design specifications and target quantities [110]. Conditions and yields are shown in Table 16 for fixed-bed and fluidized-bed operations. The product has the properties of premium unleaded gasoline [68]. The content of durene (1,2,4,5-tetramethylbenzene), which can crystallize in the engine, is kept below 5 wt % by regulating reactor conditions.

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2.4. Dimethyl Ether (DME) (see also → Dimethyl Ether)

Dimethyl ether is a new promising substitute fuel for gas turbines, for LPG, and perhaps more importantly, as an alternative diesel fuel. DME has found use as a substitute propellant for the ozone depleting chlorofluorocarbons presently being phased out. The world production (1999) is around 150 000 t/a. The manufacturing process today is based on simple dehydration of methanol. The relatively small quantities of DME produced do not justify investment in new more expensive and sophisticated production facilities yielding higher volumes and lower unit prices. However, recent studies have shown that DME has the potential of being a new significant energy carrier in the future global energy market similar to liquefied natural gas.

DME can be manufactured from nearly all carbon-bearing substances at a price not much above that of standard diesel [114], [115]. DME production from natural gas is outlined in [116–118]. A brief discussion of the production process from coal derived synthesis gas follows. Coal gasification generates a fairly impure synthesis gas, which has to be cleaned thoroughly. The purification of such gas may be done by hot gas cleaning at around 400 °C in order to conserve energy. The conversion of synthesis gas directly through methanol into DME takes place in a synthesis loop consisting of three catalytic fixed-bed adiabatic reactors with indirect cooling. The catalyst applied is a proprietary dual-function catalyst, catalyzing both steps (i.e., methanol and DME synthesis) in the sequential reaction. Significant advantages arise by permitting the methanol synthesis, the water–gas shift, and the DME synthesis reaction to take place simultaneously. The synthesis of DME from synthesis gas involves three reactions:

$$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O \quad \Delta H = -50.1 \text{ kJ/mol} \qquad (5)$$

$$H_2O + CO \rightarrow H_2 + CO_2 \quad \Delta H = -40.9 \text{ kJ/mol} \qquad (6)$$

$$2\,CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad \Delta H = -23.4 \text{ kJ/mol} \qquad (7)$$

Reactions (5) and (6) represent a conventional methanol synthesis. This methanol synthesis is restricted by equilibrium, which requires high pressure in order to reach an acceptable conversion. The introduction of Reaction (7), the DME synthesis, serves to relieve the equilibrium constraints inherent to the methanol synthesis by transforming the methanol into DME. Moreover, the water formed in Reaction (7) is to some extent driving Reaction (6) to produce more hydrogen, which in turn will drive Reaction (5) to produce more methanol. Thus, the combination of these reactions results in a strong synergetic effect, which dramatically increases the synthesis gas conversion potential.

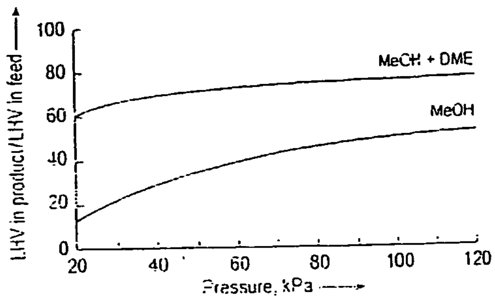

Figure 10. Conversion of C + CO_2 at equilibrium as a function of synthesis pressure for a typical synthesis gas composition

Figure 10 shows the conversion of CO + CO_2 at equilibrium as a function of synthesis pressure for a typical synthesis gas composition. The efficiency of the process and the dual-function catalyst have been demonstrated in a 50 kg/d process demonstration pilot in Haldor Topsøe's facilities in Copenhagen, Denmark. The original catalyst charge has been in operation for more than 15 000 h and demonstrated an excellent stability with an aging profile slower that the of commercial methanol synthesis catalysts.

Subsequently to the start up of the Topsøe pilot plant, Air Products of USA and NKK of Japan have piloted the synthesis of DME from synthesis gas based on slurry bed reactors [119].

NKK began working to develop the direct synthesis technology for DME in 1989 and has established a 50 kg/d bench plant. In 1997, NKK started an R&D project on direct synthesis technology for the low cost mass production of DME using a 5 t/d pilot plant to evaluate the whole system. The basic features of the NKK process are its slurry bed and its newly developed catalyst system which realize the direct reaction (Eq. 8)

of synthesis gas with a H_2 : CO ratio of 1 in the slurry phase. NKK uses a slurry bubble column reactor with an inner diameter of 90 mm and a height of 2 m. The hybrid catalyst containing $CuO-ZnO/Al_2O_3$ and copper-modified γ-alumina showed a high activity for the synthesis of DME in the slurry phase. Optimum synthesis gas conversion (56 %) and high selectivity to DME (98 %) were achieved at the initial H_2 : CO ratio of 1 [120–123]:

$$3\,CO + 3\,H_2 \rightarrow CH_3OCH_3 + CO_2 \quad \Delta H = -246.1\ kJ/mol \qquad (8)$$

Coal-derived synthesis gas obtained by high-temperature gasification has a H_2 : CO ratio of 0.5 to 1, which has to be adjusted to $H_2 : CO = 2$ by an expensive shift converter before the DME synthesis in order to synthesize DME according to Equation (7). The reaction according to Equation (8) has a substantial advantage regarding synthesis gas preparation and DME conversion [124].

With funds provided by the Agency of Natural Resources and Energy of the Ministry of International Trade and Industry, the Center for Coal Utilization of Japan, Japan is conducting a five year project to evaluate the whole system of the direct synthesis of DME. The project started in the fiscal year 1997 with the cooperation of NKK, Taiheiyo Coal Mining Co., Ltd. and Sumitomo Metal Industries, LTD. In 1999, a 5 t/d pilot plant was constructed at Taiheiyo Coal Mining's site in Kushiro, Hokkaido and the operation was started. The dimensions of the slurry phase reactor are 55 cm inner diameter and 15 m height. The aimed single-pass synthetic gas conversion is around 50 % [124].

2.5. Environmental Protection

Liquefaction plants, like SASOL in South Africa, produce gaseous, liquid, and solid effluents. Emissions into the environment are controlled by integral plant design technologies, some of which are used in related industries, such as utilities or petroleum refining.

Atmospheric pollutants arise from (1) burning coal and fuel gases (2) gasification, (3) coal handling and preparation, and (4) fuel refining. *Combustion-generated pollutants* from the steam and utilities plant are primarily particulates, sulfur dioxide, nitrogen oxides, and volatile organic compounds. Other inorganic pollutants are found in coal, including fluoride, beryllium, lead, and mercury. The known technology for controlling pollution created by coal combustion is, of course, applicable here. Flue gas desulfurization (FGD) units [125], electrostatic precipitators (ESP), and bag houses [126] can be used to control sulfur dioxide and particulates. Nitrogen oxides (NO_x) emissions can be minimized by combustion techniques or chemically [127], for example with Thermal DeNox. The ash and sulfur contents depend on the characteristics of the coal. In the United States, regulations currently exist for coal-fired utilities but not as yet for coal conversion plants; these regulations will most likely be extended as needed [128]. With appropriate design, indirect liquefaction plants can eliminate coal combustion for steam and utilities production. If gasifiers process feed coal, including fines, all the steam and power requirements could be met by combustion in gas turbines of a portion of the cleaned synthesis gas.

The crude gasification product contains almost 100 % of the coal sulfur, mostly as hydrogen sulfide. The sulfur content must be reduced to ca. 1 mg/kg so as not to poison the catalyst. Various processes convert the hydrogen sulfide to elemental sulfur, which is marketable. The most common of these are the Stretford, used at SASOL, and the Claus process, used at several petroleum refineries. The Stretford process was developed by BGC and is used worldwide in over 50 plants [77], [78].

The Claus process has been well established in the refinery and natural gas industries for many years. Several hundred plants operate worldwide, with an average capacity of 100 t/d of sulfur. The correct stoichiometric portion of feed H_2S is oxidized by combustion in a front-end furnace to yield SO_2, which oxidizes the remaining H_2S in downstream catalytic reactors:

$$2\,H_2S + 3\,O_2 \longrightarrow 2\,H_2O + 2\,SO_2$$

$$2\,H_2S + SO_2 \longrightarrow 2\,H_2O + 3\,S$$

Residual sulfur compounds can be removed by the Shell Claus Offgas Treating (SCOT) process